SOME PROPERTIES OF ZINC CHLORIDE IN WATER - ETHYL ALCOHOL MIXTURES.

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Thesis for the Degree of Doctor of Philosophy.

1932

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SECTION I.

Section 1.

The Free Energies of Zinc Chloride in Water - Ethyl Alcohol Solutions.

Introduction.

The properties of an electrolyte in a pure solvent are very largely governed by the dielectric constant and the viscosity of the pure solvent. In a mixed solvent, however, there is the possibility that the solute ions may exert a differential attraction on the two kinds of solvent molecules and in such cases the properties of the solute will not be determined by the mean properties of the solvent. Studies of the properties of electrolytes in mixed solvents may therefore provide information as to the specific interactions between the ions of the solute and the two kinds of solvent molecules.

A few years ago Butler and Robertson published a paper [Proc. Roy. Soc., *A*, 125, 694, (1929)] on the free energies and heat contents of hydrogen chloride in water - ethyl alcohol solutions. As a result of their measurements they came to the conclusion, that, in solutions containing only a small proportion of water, the latter was largely associated with the electrolyte. In view of this result it seemed desirable to carry out a similar series of investigations with a typical salt in order to ascertain

whether it would behave in an analogous manner. From the point of view of simplicity, a uni-univalent salt such as lithium chloride should be selected. Accordingly, a series of measurements with cells of the type

Li amalgam	Li Cl (m) water-alcohol	Ag Cl (s)	Ag

was commenced [Butler and Lees (unpublished research)] but it was found that reliable values could not be obtained with the lithium amalgams in alcoholic solutions. A similar experience with sodium amalgams is recorded by Wolfenden, Wright, Ross Zane and Buckley, [Trans. Faraday Soc., No77, Vol.XXIII p.491 (1927)]. Calcium chloride is sufficiently soluble in alcohol for the purpose, but the behaviour of calcium amalgams in alcohol has been found by Scatchard to be uncertain. (Private Communication). Zinc chloride appeared to be a suitable salt for an investigation of this type for it is sufficiently soluble in alcohol and water, and possesses the advantage that various investigators have worked successfully with zinc electrodes in aqueous solution

Jahn[Wied.Ann., 28, 21 (1886)] has made a few measurements of the electromotive force of the

cell

$$Zn\ (s) \left| \begin{matrix} Zn\ Cl_2\ (m), \\ water \end{matrix} \right| Ag\ Cl\ (s) \Big| Ag$$

in water at 0° using an amalgamated zinc rod as the zinc electrode, while Horsch [J.A.C.S., 41, 1787, (1919)] has measured the E.M.F. of this cell at 25° from very low concentrations up to .01 molal. His electrode consisted of finely divided zinc, attempts to use an amalgam electrode having met with failure, probably since air was not excluded. A series of measurements on similar cells using two-phase zinc amalgams have been performed by Scatchard and Tefft [J.A.C.S., 52, 2272, (1930)] while Kahlenberg [J. Physic. Chem 5, 379, (1899)] has measured the electromotive force of the combination

$$Zn\ (s) \left| \begin{matrix} .05N\ Zn\ Cl_2 - \\ water. \end{matrix} \right| Normal\ Calomel\ Electrode$$

It appears, however that little work with zinc electrodes and zinc chloride has been done in alcoholic solutions. The combinations

$$Zn\ (s) \left| \begin{matrix} 0.05N\ Zn\ Cl_2 - \\ ethyl\ alcohol \end{matrix} \right| Normal\ Calomel\ Electrode$$

and

$$Zn\ (s) \left| 0.05N\ Zn\ Cl_2\ in\ ethyl\ alcohol \right| \begin{matrix} 0.05N\ Zn\ Cl_2 \\ in\ water \end{matrix} \Big| Zn$$

have been investigated by Kahlenberg (Loc. Cit.) while Jones and Smith [Amer. Chem. J. 23, 377, (1900)] measured the electromotive force of the cell

Zn	0.1N $ZnCl_2$ in ethyl alcohol	:	0.1N $ZnCl_2$ in water	Zn.

The potentials of zinc in aqueous and alcoholic solutions of zinc chloride have been determined by Getman and Gibbons [Amer. Chem. J., 48, 124, (1912)] by measuring the electromotive force of cells of the type:-

Zn (s)	$ZnCl_2$(m) water, methyl or ethyl alcohol	Normal Calomel Electrode.

Zinc amalgams have been used by various investigators and very accurate measurements on the electromotive force between zinc amalgams have been made by Richards and Forbes. [Carnegie Institute Pub., No 56 (1906)]. These authors describe a useful method of handling and preserving the amalgams so that reliable results may be obtained. So far as the author is aware, no work has been done with zinc amalgams in alcoholic solution.

On the other hand, there are several disadvantages possessed by zinc chloride for an investigation of this nature. In the first place, it is not a simple valence type, and the theoretical behaviour of such salts has not been so thoroughly explored as that of uni-univalent salts. Again, it was not known to the author at the commencement of this investigation that, while zinc chloride is a strong electrolyte in water, it becomes a very weak electrolyte or non-electrolyte in alcohol. [Getman and Gibbons, Loc. Cit.] . However, although it is doubtful whether

the case of zinc chloride throws much light on the behaviour of typical strong electrolytes, nevertheless zinc chloride possesses an interest of its own, particularly as illustrating the transition with continuous change of solvent composition from a strong to a very weak electrolyte.

In this section an account is given of measurements of the electromotive forces of cells of the type

Zn 1 per cent amalgam	$ZnCl_2$ (m) AgCl (s) water - alcohol	Ag

The free energy change in the cell reaction

$$Zn + 2\,AgCl\,(s) \longrightarrow ZnCl_2\,(m) + 2\,Ag$$

is given by

$$\Delta F = -\,2\,EF = -\,46{,}148\,E \text{ calories},$$

where E is the electromotive force and F the electrochemical equivalent.

The electromotive forces of this cell were determined at 15°C. using a series of solvents containing 0, 25, 50, 90, and 100 moles per cent alcohol and in each solvent a series of zinc chloride concentration up to m=1. (Throughout these pages m is the number of gram-molecules of zinc chloride in 1000 grams of solvent.)

It may be mentioned here that it was originally intended to measure the E.M.F. of the cell at 15°,

25°, and 35°, so as to obtain the temperature coefficients. When several runs had been performed at 15° however, it was found that the behaviour of the cell made it extremely doubtful whether the desired accuracy of measuring the temperature coefficients could be attained by this method. The idea was therefore abandoned, and the remainder of the measurements were made at 15°.

The free energy of transfer of zinc chloride from a solution (1) to a solution (2) is given by

$$\Delta F\ (1) \longrightarrow (2) = -2\,(E_2 - E_1)\,F \qquad (2)$$

We can thus obtain from the electromotive forces the free energies of transfer of zinc chloride

(1) in a given solvent from one concentration to another.

(2) at a given concentration from one solvent to another.

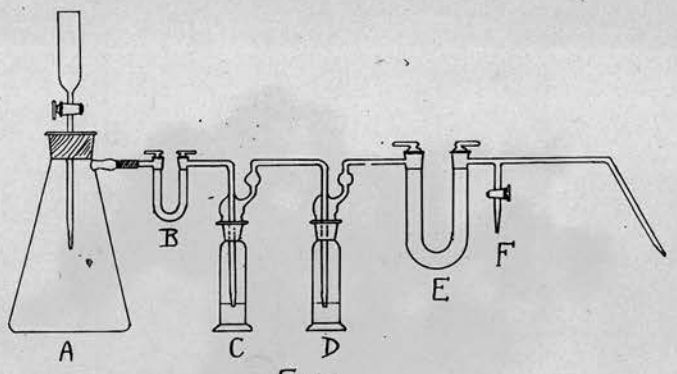
Experimental.

1. Preparation of Materials and Electrodes.

Alcohol. Commercial absolute alcohol which had been allowed to stand over freshly burnt lime for at least ten days in 4 litre flasks which were shaken every day [Danner, J. Amer. Chem. Soc., 44. 2832 (1922)] was refluxed on the water bath for eight hours and then slowly fractionated, rejecting the first and last portions of the distillate. During the drying process and the fractionation, all corks were covered with tinfoil, and all outlets to the air were closed by calcium chloride tubes. The product was stored in amber-coloured winchesters. This method of purification has been used for some time in this laboratory and has been found to yield a very pure product.

Zinc Chloride. Some difficulty was encountered in finding a method suitable for the preparation of pure anhydrous zinc chloride in quantity. Baxter and Lamb [Amer. Chem. J. XXXl 229 (1904)] prepared the pure anhydrous substance by heating the double salt $ZnCl_2 3NH_4Cl$ in a current of dry hydrogen chloride until all the ammonium chloride was removed. This method was tried but, owing to the difficulty of entirely removing ammonium chloride and simultaneously avoiding the volatilisation of

the remainder of the substance, it was found to be unsuitable for the preparation of large quantities. In the search for a suitable method it was found that pure dry zinc dissolves in a solution of pure dry hydrogen chloride in dry ether. Accordingly the zinc chloride was prepared as follows.
20 to 30 gms. of A.R. zinc which had been dried in an oven and stored over phosphorus pentoxide were placed in a 250cc. flask. The flask was provided with a short bent delivery-tube entering the flask through a ground-in glass stopper and drawn out to a fine jet at the other end. About 100ccs. of ether which had been dried over sodium wire for some time and finally distilled, were added and pure dry hydrochloric acid gas was passed in. The gas was generated and purified in the apparatus shown. Fig.1. The only rubber in the apparatus is the stopper of the flask A and the connection from A to the remainder of the apparatus. The hydrogen chloride was generated in A by dropping concentrated sulphuric acid on a mixture of A.R. sodium chloride and A.R. hydrochloric acid. The U-tube B contained glass beads moistened with a saturated solution of pure copper sulphate in order to remove any hydrogen sulphide which might be introduced by the rubber.



- Fig 1 -

Apparatus for preparation and purification of Hydrogen Chloride

The gas was dried by passing through pure concentrated sulphuric acid in the wash bottles C and D and finally passed to the U-tube E of which the limb nearest D contained phosphorus pentoxide while the other limb was packed with glass wool in order to remove any particles of phosphorus pentoxide which might be carried over in the gas. F is a trap, provided in case any ether was sucked back at any time into the delivery tube.

It was found that the zinc dissolved very slowely until the ether became saturated with hydrogen chloride, when solution proceeded rapidly. When most of the zinc had dissolved, the flask was removed from the gas supply, the stopper inserted, and the flask was set aside until the whole of the zinc had dissolved, hydrogen escaping through the jet of the delivery tube. The liquid in the flask was now perfectly clear and generally consisted of two layers, the upper being mobile and probably consisting of a solution of zinc chloride in ether, while the lower was viscous and was probably a solution of ether in zinc chloride. The delivery-tube was now connected to the vacuum pump and the flask warmed gently on a water bath when the ether and excess of hydrogen chloride were removed leaving pure anhydrous zinc chloride in the flask. This

was stored in a vacuum desiccator over phosphorus pentoxide. Zinc chloride prepared by this method is a white, excessively hygroscopic, powder which dissolves in water, alcohol and ether giving a perfectly clear solution. Getmann & Gibbons (Loc. Cit) mention difficulties due to hydrolysis of zinc chloride in dilute solution. The author, however, has not noticed this with zinc chloride prepared by the above method. In fact it is the writers' experience, that, provided zinc of known purity is used, the clearness of the solution may be used a criterion of the purity of the product.

In a preliminary experiment 4.384 gms. of zinc yielded 9.113 gms. of zinc chloride. The weight calculated from the formula $ZnCl_2$ is 9.141 gms.

A volumetric chloride analysis yielded the result:-

Percentage Chlorine - 51.8

Percentage calculated from formula 52.0

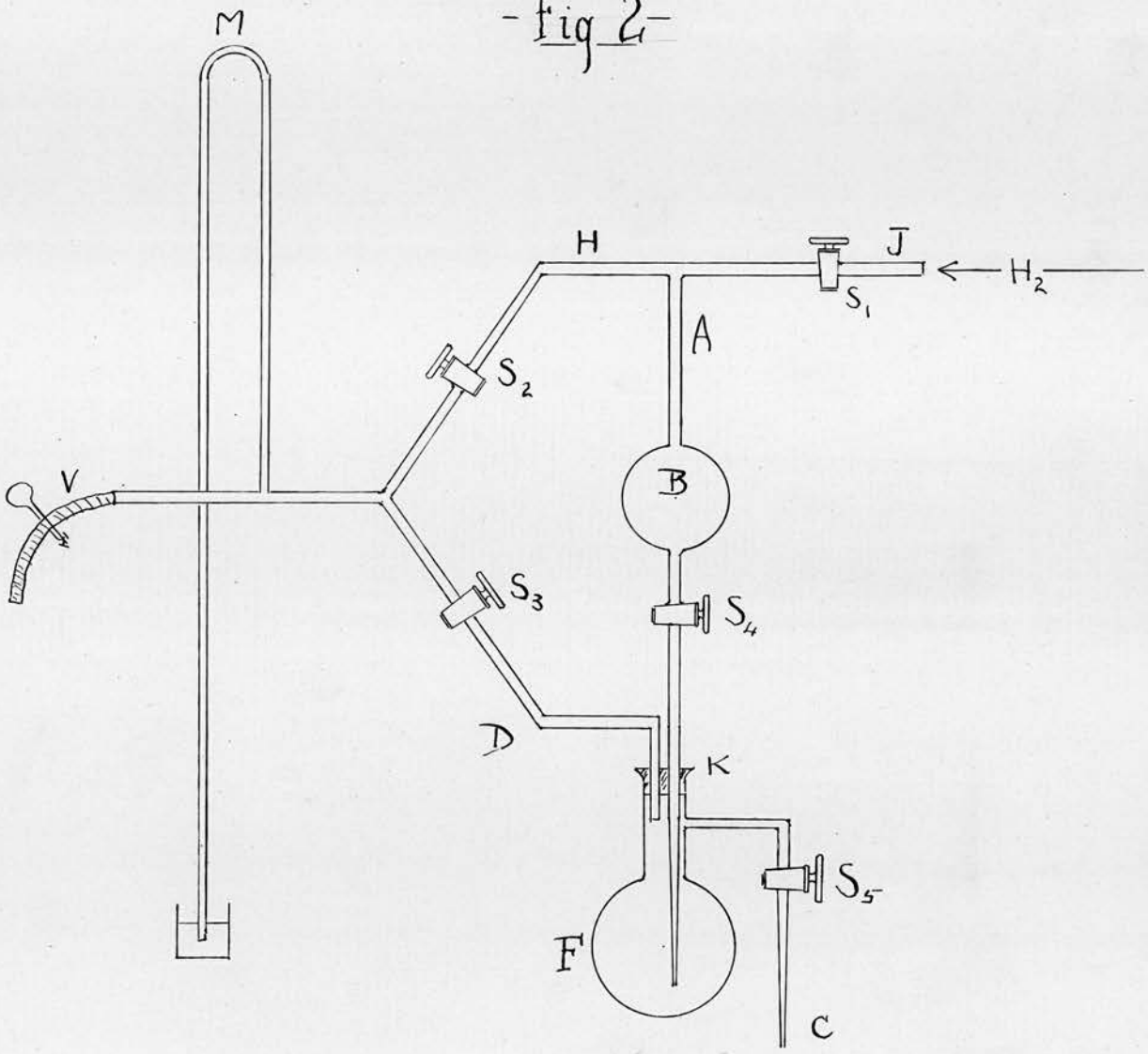
It is evident from the figures that the zinc chloride prepared by this method is sufficiently pure. In the later work ether which had been prepared from rectified spirit was used instead of ordinary commercial ether in order to ensure that a product of uniform high purity was always obtained.

Zinc Amalgams:- The mercury used in the preparation of the amalgams had been well washed by running it, in the form of small drops, several times down a column of dilute nitric acid. It was then dried and twice distilled in a current of air, under reduced pressure.

Pure electrolytic zinc was obtained in the following manner. Pure ammonia gas generated by boiling A.R. ammonia solution was passed into a strong solution of A.R. zinc sulphate until the heavy precipitate of zinc hydroxide had dissolved. This solution was then electrolysed, the cathode consisting of a number of platinum wires sealed into glass tubes. Using a fairly high current density, crystals of zinc grew rapidly on the cathodes. Gentle shaking removed the crystals which were, from time to time, withdrawn to a beaker containing dilute ammonia. When sufficient zinc had collected, it was washed with dilute ammonia, water, pure alcohol and ether and was left in a desiccator over night. The amalgam was then prepared and sealed up clean and dry in an atmosphere of hydrogen by the method of Richards and Forbes (Loc. Cit., p. 18). Since it is difficult to combine dry zinc with mercury without heating, these must be shaken together under some reagent capable of dissolving the superficial film of /

oxide, such as dilute ammonia. The amalgam was therefore made by weighing out suitable portions of zinc and mercury into a stoppered bottle, adding a little pure dilute ammonia and shaking vigorously until the zinc had dissolved. The amalgam made up by this method was separated from the ammonia and sealed up clean and dry by the aid of the apparatus shown in Figure 2. The hydrogen was prepared from pure "As T" zinc and hydrochloric acid (1:3) in a generator of the Richards type and was passed through three towers each 50 cms. high, containing glass beads moistened with a saturated solution of sodium hydroxide. The delivery tube was sealed to the apparatus in Figure 2 at J. The pipette B is sealed to the tube H and is drawn out to a thick walled capillary which passes through the rubber stopper K into the flask F. F is provided with a side-neck C which is also drawn out to a thick walled capillary. S_1, S_2, S_3, S_4, and S_5, are taps lubricated with a lubricant made by dissolving pure rubber in paraffin wax and vaseline and then filtering. The only rubber in the apparatus is the stopper K which was boiled with sodium hydroxide solution and then water several times before use. The tube H communicates with a vacuum pump, a

- Fig 2 -



- Device for preparing Amalgams -

manometer M being included. When the apparatus had been thoroughly cleaned and dried it was filled with hydrogen by the following process. With taps S_1, S_2 and S_5 closed and S_3 and S_4 open, the pressure in B and F was reduced to 1 or 2 cms. of mercury and the rubber tube V closed, in order to test for leakage. When any defect of this nature had been remedied S_3 was closed and the apparatus allowed to fill with hydrogen by cautiously opening S_1. This was performed three or four times after which S_5 was opened and a stream of hydrogen allowed to issue from C. The tube C was now plunged below the surface of the amalgam, S_4, S_5 and S_2 were closed and S_3 opened, exhausting F. On opening S_5 the amalgam was sucked into F, S_5 being closed just before the last of it enters F. On opening S_4 leaving S_3 open a rapid stream of hydrogen under reduced pressure was bubbled through the amalgam in F to mix and dry it thoroughly. After five or ten minutes S_3 was closed and F allowed to fill with hydrogen, S_1 and S_4 were closed and B was evacuated through S_2. Then S_4 was cautiously opened and the amalgam sucked into B, filling not more than 10 per cent of the entire volume. On closing S_4 and S_2, B filled with hydrogen, the pump was disconnected and S_2 opened so that hydrogen

escaped at V. A was now sealed off, tube D cut, and the pipette with the amalgam was detached and placed in a rack, the tip of the capillary being closed with wax.

The amalgam prepared in this way remained clean and bright and, in fact, what remains of it is still in this condition. When some of it was required, all that was necessary was to melt the wax on the capillary tip and open the stop-cock, the weight of the amalgam being sufficient to permit its withdrawal.

Silver-Silver Chloride Electrodes - See p. 15.

Silver-silver Chloride Electrodes: Previous work on silver electrodes by the author, in conjunction with Mr G. Armstrong (unpublished) had indicated that electrodes which had been plated in a potassium silver cyanide solution were no more reproducible than those plated in silver nitrate solution while they remained constant for a much shorter time than the latter probably owing to adsorption of cyanide ion. It was therefore decided to avoid plating in a cyanide solution.

Platinum gauze electrodes were plated in a solution of pure ammoniacal silver nitrate for 4 hours using a current of 6 milliamperes per electrode. After thorough washing they were coated with a stiff paste of pure silver oxide and distilled water and dried in an oven. They were then heated in an electric furnace for 6 hours at 450° in order to reduce the oxide to silver and finally chloridised by electrolysing in a 0.1m solution of hydrochloric acid in the solvent in which they were to be used for 5 hours with a current of 4 milliamperes per electrode. By this means electrodes were prepared which were readily reproducible to 0.1 millivolts.

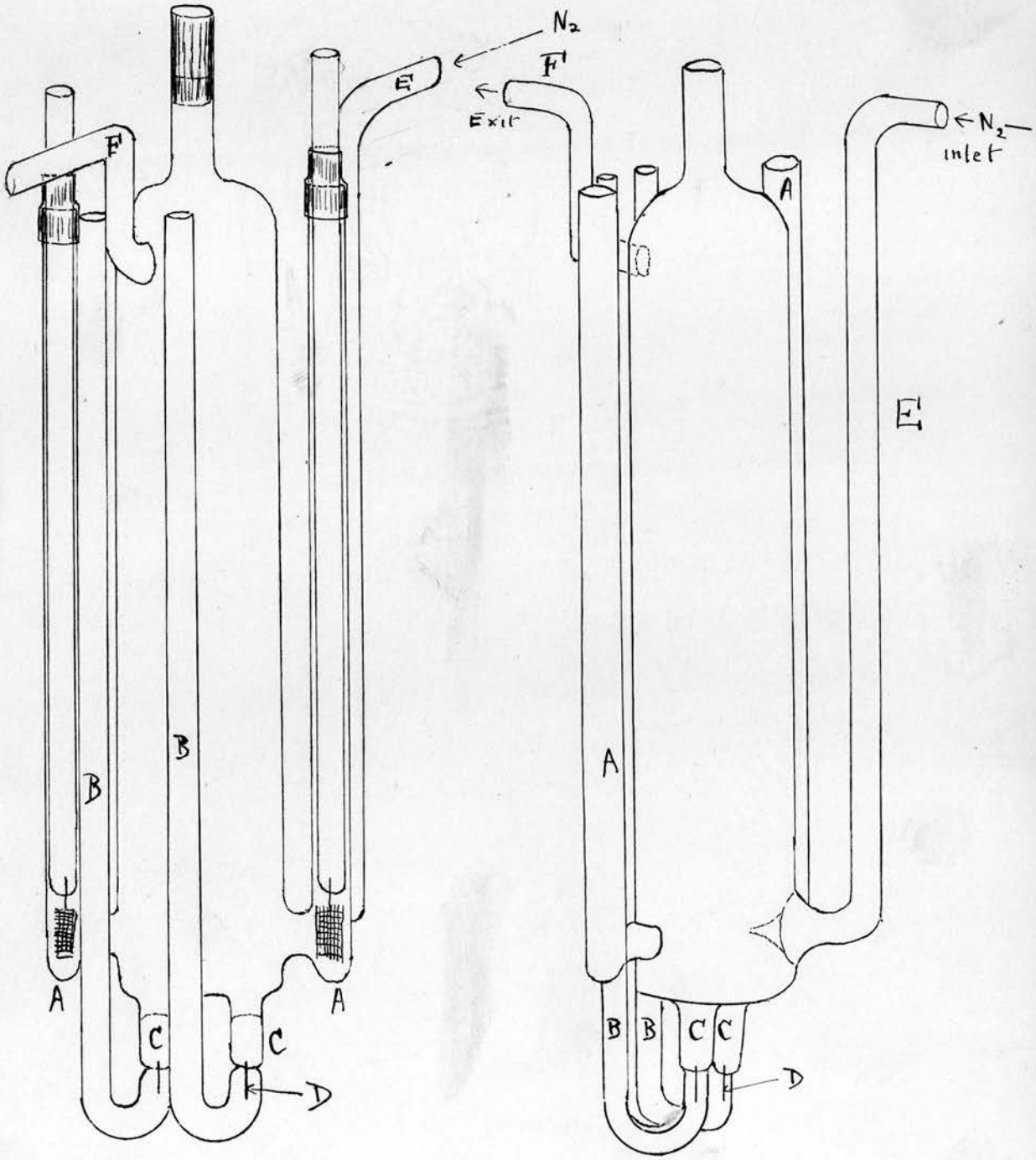
2. Apparatus and Procedure.

Since the success of measurements of this nature depends on complete exclusion of oxygen from the cell during a course of experiments the cell required to be designed to facilitate this. Several types were used, the most convenient being that shown in figure 3. The side tubes A A contain the silver chloride electrodes which are fixed in position with short lengths of clean rubber tubing. The amalgam is contained in two cups C C blown in the bottom of the cell while short lengths of platinum wire D are sealed into the base of the cups in order to afford a means of connection. Since the cell was used in the thermostat, tubes B are sealed to the base of the cups and bent upwards. Connection to the amalgams was then effected by running a little mercury into these tubes and leading wires from the potentiometer into the mercury. The tube E serves to admit nitrogen to the cell when necessary, while F was used as a convenient outlet.

For the purpose of freeing the cell and solutions from air nitrogen is preferable to hydrogen, since hydrogen affects the silver-silver chloride electrodes. (Butler & Robertson. Loc. Cit.)

The general arrangement of the apparatus used

- Fig. 3 -

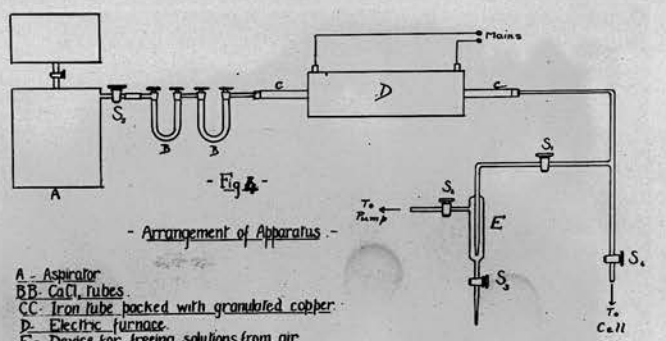


— Diagrams of Cell. —

in filling the cell and in freeing the solutions from air is shown in figure 4.

The Aspirator was filled with nitrogen from a cylinder. After passing through the drying tubes B B the gas entered a long iron tube which was packed with copper turnings for about a metre of its length. The tube passed through an electric furnace which was used to heat the copper to a sufficiently high temperature to remove any oxygen which might be contained in the gas. The nitrogen, freed from oxygen as above, now entered the cell through the tap S_4 while some of it could be used for freeing the solutions from air in E.

In performing a series of experiments the following procedure was adopted. The iron tube having been allowed to heat up, taps S_1 and S_4 were opened and the apparatus, as far as these taps, cleared of air by a current of nitrogen. The device E was now connected on the other side of S_1 which, with S_4, was now closed. Tap S_3 was then closed while S_2 was opened and E was evacuated by the pump. S_2 was now closed and S_1 slowly opened, E being allowed to fill with nitrogen. When this had been repeated several times S_2 was closed and S_1 and S_3 were opened so that a slow current of nitrogen passed through the constricted tube beyond S_3. This jet was



- Fig 4 -

- Arrangement of Apparatus -

A - Aspirator
BB- CaCl2 tubes.
CC- Iron tube packed with granulated copper
D- Electric furnace.
E- Device for freeing solutions from air.
S1,S2 etc. - Taps.

now made to dip below the solution which was to be used, contained in a small beaker, and taps S_3 and S_1 were closed. By opening S_2 and, finally, S_3 carefully, as much solution as was required was sucked into E. S_3 was now closed. In this way the solution was introduced into E without admitting any air. By keeping S_2 open, and S_1 and S_3 closed, the solution was then boiled under reduced pressure for a few minutes. In this manner it was believed that most of the air dissolved in the solution was removed. Tap S_2 was closed and S_1 slowly opened admitting nitrogen until the original pressure was restored. The pump was now disconnected and, with S_2 open, nitrogen was allowed to bubble through the solution contained in E in order to displace the remaining oxygen and saturate the solution with nitrogen. Finally, taps S_2 and S_1 were closed.

The cell, carefully cleaned and dried, and containing mercury in the tubes B was now connected beyond S_4. The tubes A A and the mouth of the cell were tightly stoppered and F was connected to the vacuum pump, a manometer being included by means of a T-piece. The cell was now completely freed from air and filled with nitrogen by a process of evacuation and filling such as was used in freeing the

solution from air. The pump was then disconnected and f closed. The rubber stopper was now removed from the mouth of the cell and, with nitrogen issuing from the cell, the amalgam pipette was introduced, the fine capillary (Richard and Forbes, Carnegie Inst. Publ. no.56 p. 20) reaching to the foot of the cell, and portions were run into the cups. Previous to introduction into the cell some amalgam was rejected, and immediately after use the tip of the pipette was covered with wax so that no oxidised amalgam should be introduced into the cell. Tap S_1 was now opened and by opening S_3 the solution in E was forced into the cell, nitrogen meanwhile issuing from the mouth of the cell. During this operation the jet of E was inserted into the mouth of the cell so that the solution never came into contact with the air, and, previous to introduction into the cell, the solution, which filled the jet of E beyond S_3, was invariably rejected, since it possibly contained air reabsorbed from the atmosphere.

The stoppers were now removed from the tubes A of the cell and the silver chloride electrodes, carefully washed in the solution in which they were to be used, were inserted and fixed in position by the short lengths of rubber tubing. The stopper was then replaced and the tap S_4 closed. When all joints

had been examined the cell was placed in the thermostat. During the course of a run of experiments the cell and E were kept connected beyond S_4 and S_1 and were only disconnected at the completion of a run for cleaning. Provided that all these precautions were observed, the amalgams remained perfectly clean and bright and gave perfectly reproducible results.

When a cell had been set up in this way and found to be satisfactory, a run of measurements were made, keeping to the same solvent. When the mean electromotive force of the cell had remained constant to about 0.00005 volts for an hour, the tap S_4 was opened, the stopper removed, and a portion of the solution was withdrawn for analysis. A few cubic centimeters of solution were now introduced from E in the same manner as before and the cell sealed up again. It was never opened in the course of a run without nitrogen bubbling through the solution and issuing from the cell. Since it is more economical to start from a dilute solution and proceed to more concentrated ones this was the procedure which was usually adopted.

An approximately 0.01 m solution was first freed from air and introduced into the cell. E was then filled with an approximately 0.1m solution and this

was freed from air in the same way and run into the cell in several portions so that solutions from about 0.01m to 0.1m were measured first. Finally a solution slightly more concentrated than 1m was freed from air, and this, on mixing with that in the cell, gave solutions from 0.1m to about 1m. As a rule the electrodes remained satisfactory long enough for the electromotive forces of the cell to be determined from the most dilute to the most concentrated solutions in one run.

The method of freeing the solutions from air described above suffers from the disadvantage that in the water-alcohol mixtures the relative proportions of the two components will alter slightly as a result of boiling under reduced pressure and bubbling nitrogen. It was considered, however, that, provided the process was not carried on too long, any errors introduced from this source would be inconsiderable. Since the concentrations of the solutions were determined after the electromotive force measurements had been taken, no errors in estimating the concentration can arise through the above process.

Determination of the concentration of the solutions:- At the outset it was believed that the most convenient method of estimating the concentration of the solutions would be by means of the Zeiss interferometer.

When the instrument had been calibrated, however, with a series of solutions of known strength, it was found that the readings could not be satisfactorily reproduced. There was always the possibility of an error of one fringe which, in the case of some of the alcoholic solutions, corresponded to an error amounting to 5 per cent. The method was therefore abandoned in favour of the ordinary chemical method of chloride analysis.

A few grammes of solution were withdrawn by means of a pipette and transferred to a tared weighing bottle which was immediately reweighed. The amount of zinc chloride in this known weight of solution was then determined in the usual manner by precipitating the chloride with an excess of standard silver nitrate, filtering, and back titrating the excess of nitrate with ammonium thiocyanate, previously standardised against the silver nitrate. For the most dilute solutions, centinormal solutions were used, while decinormal solutions were employed for greater concentrations. This method gave results reproducible to 1 in 1000.

The electromotive forces were measured by means of a Tinsley Vernier potentiometer reading directly to 0.01 millivolt. The standard Weston cell used

was compared against one which had been recently standardised by the National Physical Laboratory. In order to avoid thermo-electric effects Constantan D.C.C. wire was used for the leads, while the thermostat was earthed, in order to avoid stray currents from the thermostat heating circuit. The potentiometer was also placed on a metal plate which was kept earthed.

The thermostat was electrically heated and controlled and the temperature remained constant to $\pm .01^{\circ}$.

The measurements were made at 15°C.

Experimental Data.

The following table gives the actual electromotive forces determined in one experiment, the silver-silver chloride electrode forming the positive pole of the cell.

Table 1.

Cell:-

Zn 1% amalgam | 0.4105 m $ZnCl_2$ in 25 mol. per cent alcohol | AgCl (s) | Ag

E.M.F.s in volts.

Time from insertion in thermostat	Electrodes.			
	1 - 3	1 - 4	2 - 4	2 - 3
hours 2	1.00661	1.00650	1.00646	1.00654
2½	1.00682	1.00680	1.00676	1.00680
3	1.00684	1.00680	1.00680	1.00682
3½	1.00684	1.00682	1.00680	1.00682

The means of the final measurements on each solution are recorded in Table 11.

Table II.

Electromotive forces in volts of the cell

Zn (1% amalgam) | $ZnCl_2$ (m) at 15°C. | AgCl (s) | Ag

Water.

m	E
.009625	1.1568
.03040	1.1180
11011	1.0799
.1031	1.0793
.1444	1.0678
.3590	1.0387
.5285	1.0261
1.202	1.0007

25 moles% alcohol.

m	E
.003490	1.1157
.006654	1.0940
.006881	1.1004
.01218	1.0813
.02611	1.0634
.07131	1.0396
.2810	1.0139
.4105	1.0068
.4925	1.0041
.7447	0.9965

50 moles% alcohol.

m	E
.002115	1.0839
.02451	1.0431
.04656	1.0314
.09199	1.0193
.1331	1.0177
.2479	1.0061
.4326	0.9988
.4475	0.9981
.7099	0.9894
1.1950	0.9788
1.4490	0.9722

90 moles% alcohol

m	E
.02555	1.0167
.04244	1.0061
.08158	0.9998
.1000	0.9974
.1703	0.9909
.4033	0.9766
.5989	0.9705
.8044	0.9649

100 moles% alcohol

m	E
.01263	1.007
.02997	1.001
.08820	0.9888
.2176	0.9783
.3178	0.9745
.4616	0.9653
1.047	0.9521

The results for aqueous solutions show satisfactory agreement with those obtained by Horsch [J.A.C.S. 41, 1787, (1919)] and by Scatchard & Tefft (Loc. Cit.) For example, Horsch's measurements yield, by graphical interpolation, the value E = 1.1588 volts when the electrolyte is .009625 molal, while the value obtained by the author for this solution is 1.1568 volts. The difference of 2 millivolts may be ascribed to the fact that Horsch worked at 25° and used finely divided zinc as the zinc electrode. The results of Scatchard and Tefft are seen (Figure 5) to lie on a curve which is from 1 to 1.5 millivolts higher than the writer's. These investigators also worked at 25° and used two-phase amalgams.

Good agreement was obtained between results in successive runs in water and the mixed solvents provided that the concentration was greater than, or equal to, about 0.01m. In more dilute solutions, however, the results were reproducible only to about 1 or 2 millivolts, the difficulty of reproducing results increasing with dilution. In the case of pure alcohol, data for hundredth and fiftieth molal solutions may contain errors of ± 2 millivolts, this error becoming less as the concentration increases.

Similar experiences are recorded by other investigators working in aqueous solutions. Horsch places a possible error of ± 2 millivolts on his measurements in solutions of concentration less than .001 molal while Getman and Gibbons (Loc. Cit.) working with the cell

Zn amalgamated rod | $ZnCl_2$ in water | Normal Calomel Electrode.

obtained very wide variations in the electromotive force in dilute solutions. Denham [J. Chem. Soc., 93, 41, (1908)] in a paper on the electrometric determination of hydrolysis, mentions similar difficulties with zinc chloride solutions.

The situation may be summed up by remarking that the difficulties attached to making the measurements increase as the solution is diluted, and also as the alcohol content increases. These difficulties are due, in part to the small conductivity of alcoholic solutions of zinc chloride and also to the fact that individual deviations in the amalgam electrodes make their appearance as the solution becomes more dilute. In solutions greater than about hundredth molal these factors do not interfere appreciably with the reliability of the measurements, but at dilutions greater than this, they make it extremely questionable at present, whether any confidence can

Fig. 5.

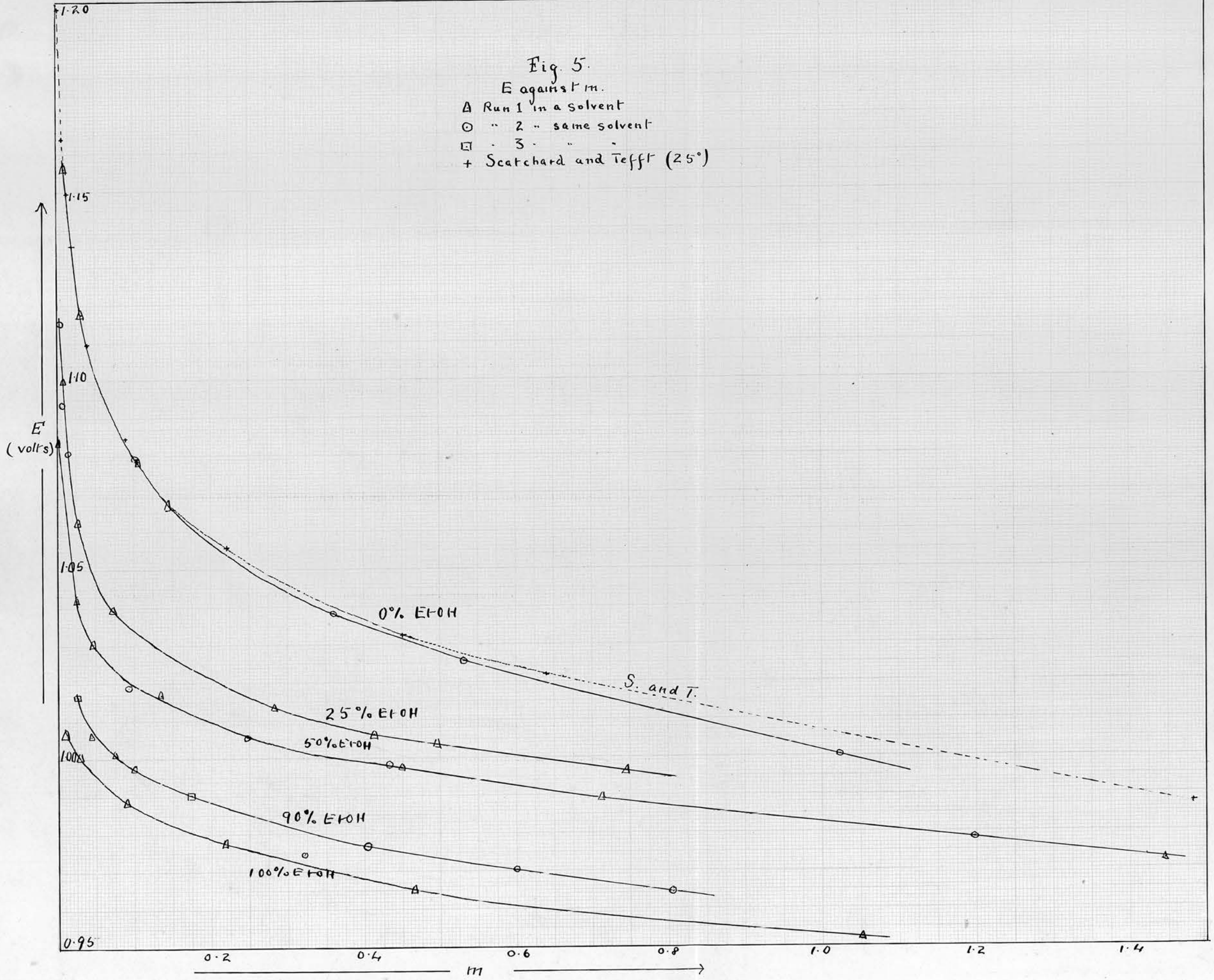
E against m.

△ Run 1 in a solvent

⊙ " 2 " same solvent

⊡ " 3 " "

\+ Scatchard and Teffft (25°)



be placed in the electromotive force measurements in these dilute solutions.

Figure 5 is a plot of the observed electromotive force against the molal concentration, while figure 6 represents the variation of the electromotive force with the logarithm of the concentration.

The free energy changes in the cell reaction are obtained by use of equation (1). These quantities are given in Table III.

Table III.

Free Energy Changes in the Cell Reaction. ($-\Delta F$).

m	Composition of solvent (moles per cent alcohol).				
	0	25	50	90	100
0.01	53301	50163	49055	47532	46517
0.05	50947	48409	47532	46379	45917
0.10	49840	47648	47071	46033	45571
0.50	47440	46333	45963	44925	44487
1.00	46494	45640	45340	44279	43979

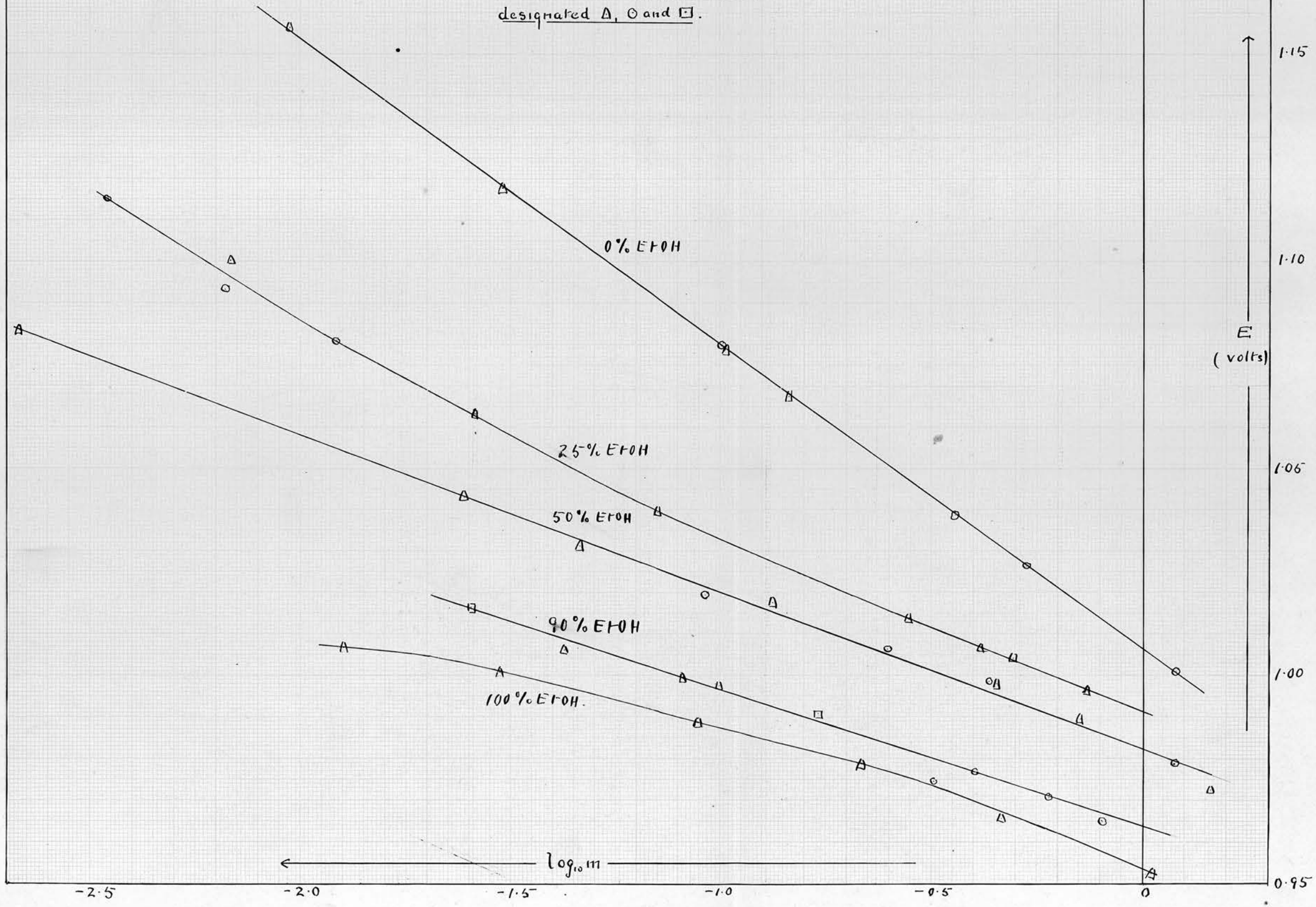
The corresponding values of E, the electromotive force, were obtained by graphical interpolation of the experimental values from figures 5 and 6.

The free energy changes in the transfer of electrolyte from one solution to the other are

— Fig 6 —

— E against $\log_{10} m$ —

Results obtained in different runs designated Δ, O and □.



readily obtained from Table III by subtracting the corresponding values.

Figure 7 shows the variation of the free energy changes in the cell reaction with composition of the solvent, the data being taken from Table III.

Discussion.

The plots of E against the logarithm of the concentration for each solvent shown in figure 6 are surprisingly close to straight lines. It may be observed that the variations from linearity are greater than experimental error. The curves of E against m are smooth and the variation of the points from the straight lines must be regarded as deviations from any such linear relationship.

A uni-bivalent electrolyte such as zinc chloride might give rise to several types of behaviour according to its degree of dissociation.

(1) If it is entirely dissociated as in the scheme

$$ZnCl_2 \rightarrow Zn^{++} + Cl' + Cl',$$

since two Faradays of electricity would be required to form three gram-ions in the solution we should have, as an ideal law, in the absence of any inter-onic attraction effects

$$E = E_0 - \frac{3RT}{2F} \log m \qquad (3)$$

or $E = E_0 - .08575 \log_{10} m$

which should be realised at extreme dilutions.

(2) If it is dissociated completely according to the equation

$$ZnCl_2 \rightarrow ZnCl^{+} + Cl'$$

we should have as the ideal law

$$E = E_0 - \frac{RT}{F} \log m \qquad (4)$$

or $E = E_0 - .05717 \log_{10} m$

(3) If zinc chloride is undissociated, or practically undissociated, then, since two Faradays are required to produce one molecule in the solution,

$$E = E_0 - \frac{RT}{2F} \log m \qquad (5)$$

or $E = E_0 - .02859 \log_{10} m$

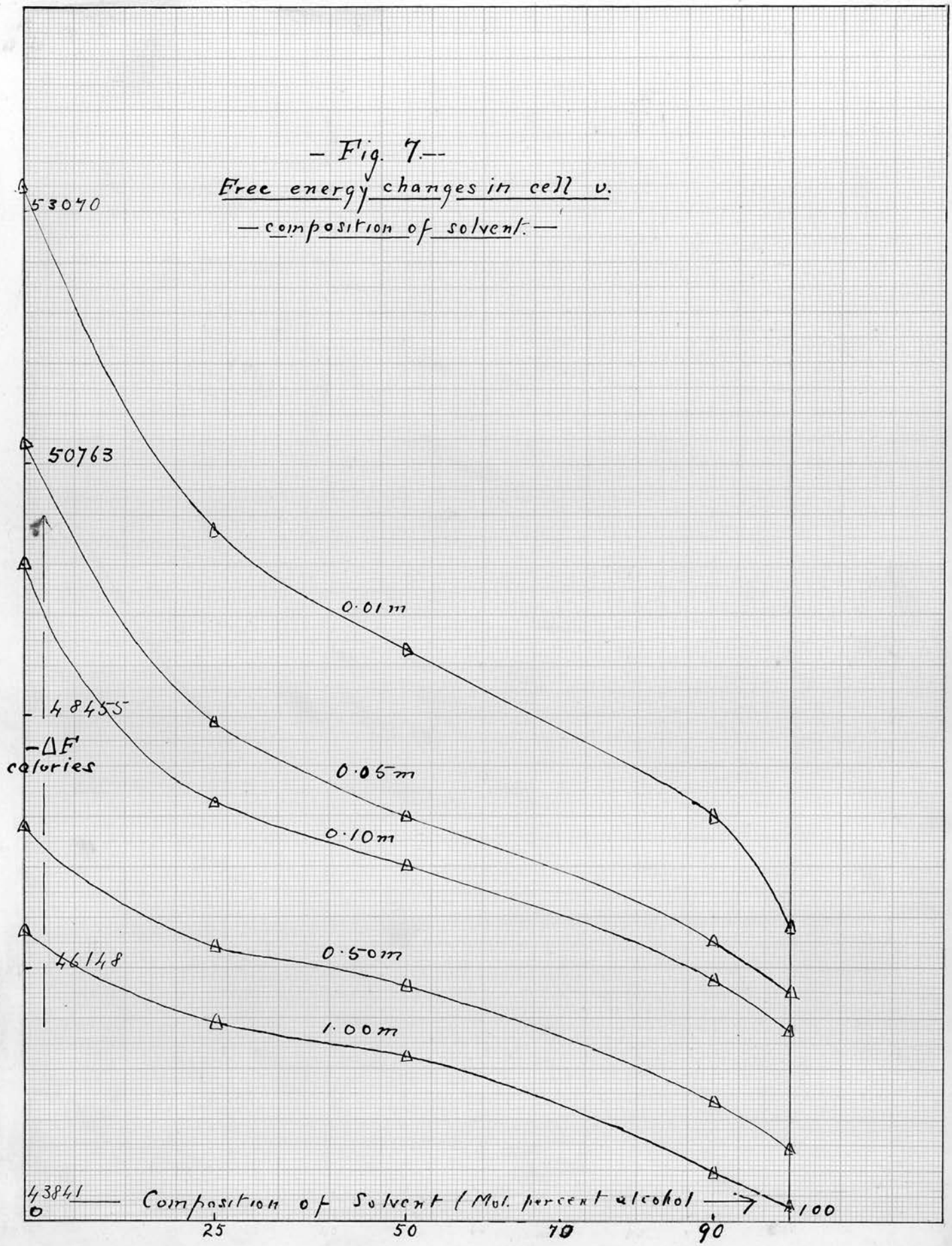
In the case of partial dissociation according to schemes (1) or (2), of course the matter will be more complicated.

The average slope of the plot of E against log m in each solvent is given in Table IV.

Table IV.

Composition of Solvent. (Moles % Alcohol)	0	25	50	90	100
Average Slope.	.0745	.0475	.03825	.034	.0280

It is evident that in 100 and in 90 moles per cent alcohol the behaviour is reasonably close to the assumption of non-dissociation. It will be shown in Section II that zinc chloride is practically a non-electrolyte in these solvents. The slopes of the other solvents are not in agreement with either of schemes (1) or (2), and it is evident that, in order


— Fig. 7.—
Free energy changes in cell v.
— composition of solvent —
53070
50763
48455
46148
43841
-ΔF
calories
0·01m
0·05m
0·10m
0·50m
1·00m
0
25
50
70
90
100
Composition of Solvent (Mol. percent alcohol →

to interpret them, it would be necessary to know the degrees of dissociation of zinc chloride in these solutions.

There is, however, one point to which attention may be directed. Figure 7 shows the variation of the free energy of zinc chloride, at constant concentration, with the alcohol content. (Since the weight concentration is used, the volume concentration in these solutions varies. The effect of varying density is, however, small compared with the other effects.)

It can be seen that the free energy ($-\Delta F$) falls rapidly with the first additions of alcohol, changes comparatively slowly in the solvents containing from 25 moles to about 90 moles per cent of alcohol and finally falls again between 90 and 100 per cent alcohol. This is markedly different from the behaviour of hydrogen chloride in the same range of solvents, as shown by Butler and Robertson (Loc. Cit.,) Now, the rapid fall at the beginning cannot be ascribed to decreasing degree of dissociation for that factor by itself would cause an increase in the value of $-\Delta F$.

Consider, for simplicity, a binary electrolyte which is completely dissociated in a solvent A and

completely undissociated in a solvent B.

Let F_S be the partial free energy of the undissociated part.

Then $F_S = F_S^\circ + RT \log m_S$ (6)

Let $F_{\bar{I}}$ be the sum of the partial free energies of the ions. Then

$F_I = F_{\bar{I}}^\circ + 2RT \log m_I$ (7)

For equilibrium it is necessary that $F_S = F_{\bar{I}}$

or $F_S^\circ + RT \log m_S = F_{\bar{I}}^\circ + 2RT \log m_{\bar{I}}$

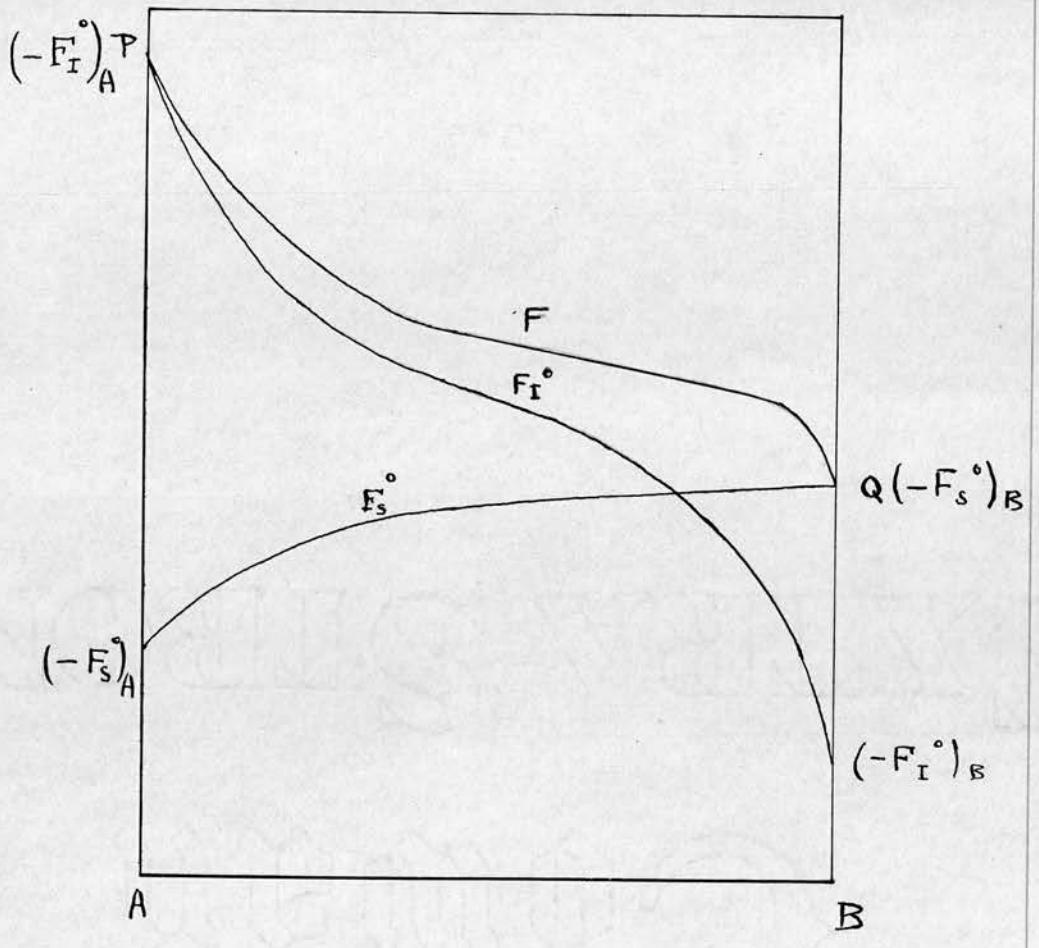
or $RT \log \frac{(m_I)^2}{m_S} = F_S^\circ - F_{\bar{I}}^\circ$ (8)

where $\log \frac{(m_I)^2}{m_S} = \log K$

K being the dissociation constant.

Now, both F_I° and F_S° may be functions of the solvent composition. If the salt is to be practically completely dissociated in the solvent A, then $(-F_I^\circ)_A$ must be considerably greater than $(-F_S^\circ)_A$ and if the salt is to be practically undissociated in solvent B, then $(-F_S^\circ)_B$ must be greater than $(-F_I^\circ)_B$. Thus we might represent the variation of these quantities with the composition of the solvent as in Figure 8. The actual form of the free energy curve in these solutions could then be constructed by the use of equation (6) or (7). The curve PQ is an approximation to the form to be expected for this particular case.

- Fig. 8. -



Conversely, it would be possible to construct the curves F_I° and F_S° from the curve F, if the degrees of dissociation in the solution were known.

The general form of the curves can be accounted for on these lines. The case of zinc chloride is, of course, more complicated, and for a quantitative explanation of the effects it would be necessary to take into account the deviations from ideal behaviour caused by the electric fields of the ions.

Summary.

(1) A convenient method of preparing pure anhydrous zinc chloride in quantity has been found.

(2) The electromotive forces of the cell

Zn			
1 per cent amalgam	$ZnCl_2$ (m) water-ethyl alcohol	AgCl (s)	Ag

have been measured at 15°C in a series of water-ethyl alcohol mixtures containing 0, 25, 50, 90 and 100 moles per cent alcohol, the concentration range extending up to 1 molal in each solvent. In the solvents containing 90 and 100 moles per cent alcohol respectively, the slopes of the lines, Fig. 6 correspond to the assumption that zinc chloride is practically undissociated in these cases.

(3) The free energy changes in the cell reaction at certain concentrations have been calculated from the electromotive force data. It has been found that the greatest free energy changes are produced by the first additions of alcohol. It has been shown that this effect cannot be due to the repression of the ionisation of the zinc chloride by the alcohol.

SECTION II.

Section II.

The Electrical Conductivities of Zinc Chloride in water-ethyl alcohol solutions.

Introduction.

In view of the peculiar features exhibited by the electromotive force data in Section I it was considered that it might be useful to determine the electrical conductivity of zinc chloride in the solvents used. It was thought that such measurements might elucidate to a certain intent the previous data.

The electrical conductivity of zinc chloride in water has been determined at 18° by Kohlrausch, [Kohlrausch and Holborn, Leitvermögen der Electrolyte (1916) p.p. 147 168.] by Heydweiller [Annalen der Physik 30, 873 (1909)] and by Long [Annalen der Physik 11, 37, (1880)] while Rabinovich [Zeit. für. Physik. Chemie 99, 338, (1921)] has made a series of determinations at 25° from 0.46 N to 22.8N. Getman & Gibbons [Amer. Chem. J., 48, 125, (1912)] measured the electrical conductivity of zinc chloride in water, methyl and ethyl alcohol at 0° and 25°, but the existence of this latter work was unknown to the author at the time of commencing the measurements. It may be mentioned, however, that the apparatus used

by these authors was not suited for measurements in dilute, non-aqueous solutions, and, while their measurements serve to indicate the general course of the conductivity curve in pure alcohol, the individual measurements show deviations among themselves much greater than any which appear among the author's measurements.

In alcohol-water mixtures a considerable amount of work has been carried out by Goldschmidt and his co-workers. This work has, however, been mainly confined to measurements on solutions of acids in mixtures of alcohols with water. For example, Goldschmidt and Aarflot [Z. physikal. Chem. 122 371 (1926)] have shown that a considerable decrease in the equivalent conductivities of strong acids in methyl and ethyl alcohol occurs when small quantities of water are added to the solvent, while Murray-Rust and Hartley [Proc. Roy. Soc., A, 126, p 84, (1929)] make the same observation for the strong acids investigated by them when 0.5% water is added to the alcoholic solutions.

There appears to be no recent accurate conductivity data for zinc chloride in ethyl alcohol or mixtures of ethyl alcohol with water.

There are certain difficulties in the way of attempting to establish any direct connection between the/

electromotive force data in Section I and the conductivity measurements. In the first place, it is impracticable to make up a mixed solvent which will accurately contain a predetermined proportion of alcohol and which, at the same time, will have a low specific conductivity, for, in order to ensure this, the solvents must be exposed as little as possible to the atmosphere. As a result of this, the data in this section are for solvents of slightly different composition from those in the first section. Secondly, concentrations in E.M.F. measurements are weight concentrations while in conductivity measurements volume concentrations are used. Hence, in order to relate the electromotive forces of cells containing given solutions to the conductivity of these solutions, the density of each solution must be determined - a procedure which would have considerably extended the work. Finally, since most recent work on the conductivities of solutions has been performed at 25° and since it was not anticipated that any direct relation between the electromotive forces of the cells and the conductivities of the solutions could be established, the measurements were taken at this temperature.

It was originally thought that it might be

possible to extrapolate the conductivity data to zero concentration and so obtain values of the equivalent conductivity at infinite dilution. The measurements were therefore extended to cover a range of concentrations from $\frac{N}{10,000}$ to N.

The following pages give an account of measurements of the electrical conductivity of solutions of zinc chloride at 25° C. in solvents containing 0, 19.64, 46.62, 89.92 and 100 moles per cent alcohol respectively, throughout the concentration range indicated above.

In this section concentrations are expressed in gram-equivalents per litre of solution.

Experimental.

(1) Preparation of Materials.

Conductivity Water:- This was prepared by the well-known method of Bourdillon. [J. Chem. Soc. 103, 791 (1913)]. The boiler was filled with distilled water to which a few grammes of potassium hydrogen sulphate had been added. The distillate had a specific conductivity which varied from 0.5×10^{-6} to 1×10^{-6} reciprocal ohms and was collected at a temperature of about 30° C. It was found that the conductivity of the distillate was not improved if the water in the boiler had been subjected to a preliminary distillation from alkali. Owing to the fact that this research was carried out during the winter months it was impracticable to carry out the distillation out of doors - a procedure which might have effected a lowering in the specific conductivity of the water. It appears, however, that the characteristics of the Edinburgh water are such as to render it impossible to obtain water of very low specific conductivity in quantity. It may be mentioned that other investigators in this laboratory obtained water of specific conductivity 0.5×10^{-6} to 1.0×10^{-6} r. ohms by distilling from alkaline permanganate in an apparatus constructed entirely of Pyrex glass. (Tait and Smith - unpublished research) but the conductivity of this/

water rapidly rose on standing. Since it was found that the specific conductivity of the water fell slightly on standing in the receiver of the still, the water was run out of the receiver by a siphon tube directly into the vessels when required and was not stored in bottles until it was to be used.

Pure Air:- Air was taken from outside and passed through concentrated sulphuric acid, concentrated potassium hydroxide solution and finally through distilled water. When the air was also required dry, the washing in water was omitted, and the pure air was then passed through calcium chloride tubes, phosphorus pentoxide and finally through glass wool to remove any phosphorus pentoxide which might be carried over.

Alcohol:- A quantity of commercial absolute alcohol which had been standing over freshly burnt quicklime for about four months was refluxed on the water bath for eight hours. It was then fractionated in an atmosphere of pure dry air by means of the following device. The receiver was closed by a rubber stopper containing three holes. One of these holes communicated with the condenser, 8-bulb fractionating column and flask by means of an adapter, while the second contained a siphon tube to which was sealed a glass tap, and the third contained a tube packed with

glass wool, calcium chloride and soda lime. This tube was connected to the supply of pure dry air. While the alcohol was heating up, the air was passed through the receiver, up the condenser and out at the head of the fractionating column. When the alcohol commenced to boil, the thermometer was inserted and the air-supply disconnected. The alcohol was then slowly fractionated. Since the receiver could not be conveniently changed without admitting air, rejection of the first portion of the distillate was performed by siphoning off successive small portions until after the boiling point had become constant. Shortly before the completion of the distillation the receiver was disconnected from the apparatus, meanwhile passing pure dry air through it, the adapter was closed by a rubber stopper and the air supply disconnected. Pure alcohol could now be run out of the receiver by means of the siphon without exposure to the atmosphere. During the distillation all corks were covered with tinfoil. In this way the alcohol was distilled and preserved in a pure dry atmosphere. The specific conductivity of the alcohol was not measured at this stage, but a day or two later, when the measurements in this solvent were performed, it was found to posses a specific conductivity of 0.029×10^{-6} reciprocal ohms.

This figure compares favourably with that given by Murray-Rust and Hartley (Loc. Cit.) for, although their alcohol when freshly distilled had a specific conductivity of 0.003×10^{-6} r.o., the conductivity of the alcohol, when used by them, varied between .014 and .065 reciprocal megohms.

Zinc Chloride:- The zinc chloride was prepared as in Section I except that ether which had been prepared from rectified spirit was invariably used. The ether was dried as before over sodium and distilled. In order to remove traces of ether the zinc chloride was heated in vacuo to about 170° using an oil bath instead of the water-bath as in Section I.

Apparatus.

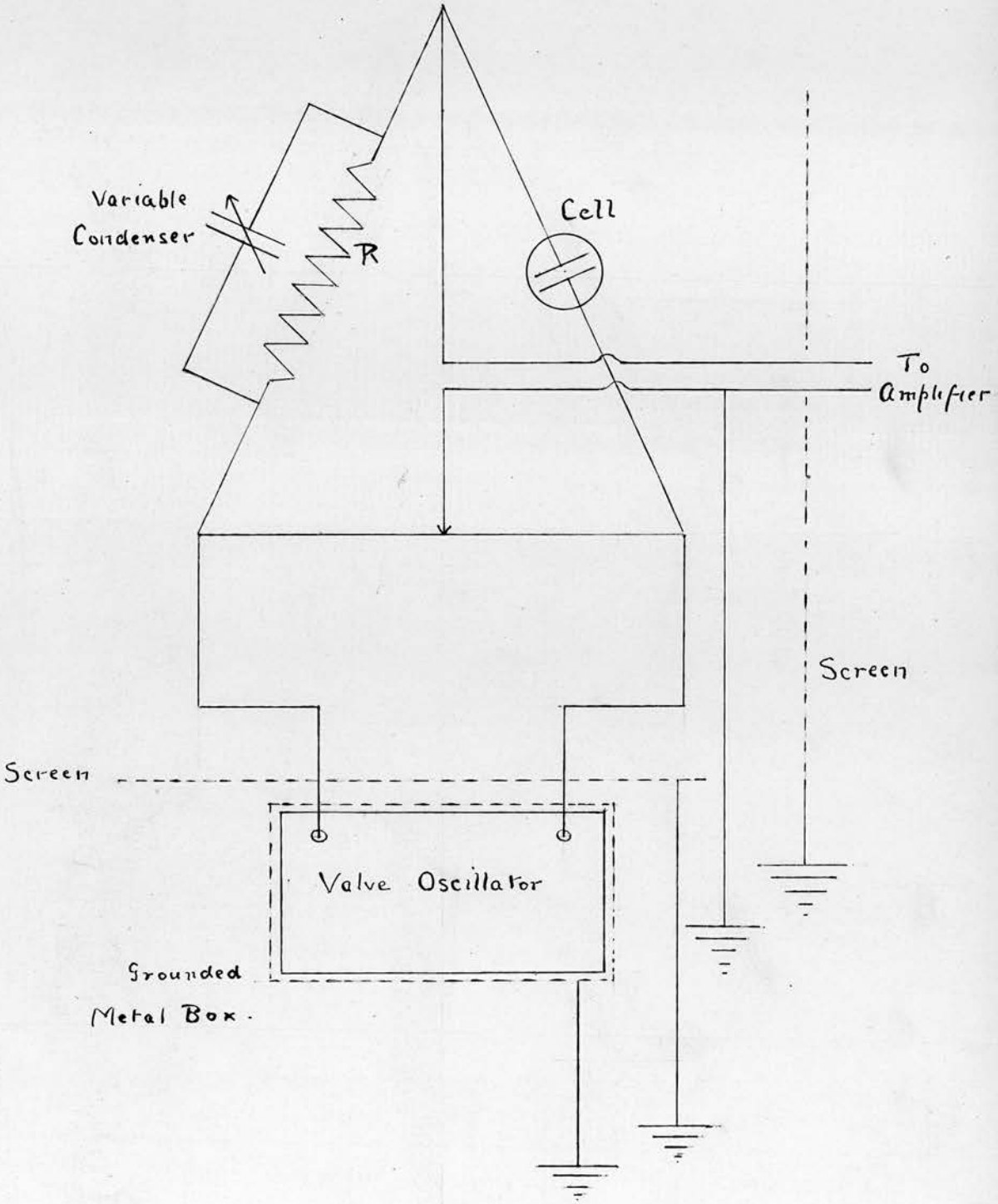
The conductivity measurements were carried out by the Kohlrausch method, the arrangement of the apparatus being shown in figure 9.

The source of alternating current was a one-valve oscillator constructed for conductivity work by the Cambridge Instrument Company.

In order to increase the sensitivity of the apparatus, a two valve amplifier was connected as shown and was so constructed that either one or two

- Fig 9. -

- Arrangement of Apparatus -



stages of amplification could be used. The oscillator and the amplifier were enclosed in grounded metal boxes and a grounded aluminium screen was placed between the oscillator and the remainder of the apparatus. The sharpness of the minimum was found to be increased by earthing the wire connected to the sliding contact of the bridge. All the measurements were made at a constant frequency of about 1000 cycles.

The available resistances consisted of an accurate specially wound non-inductive resistance box made by Tinsley giving a resistance variable in steps of 100 ohms from 100 to 11000 ohms, three certified standard resistances of 10 ohms, 100 ohms and 1000 ohms made by Gambrell and an auxiliary resistance box giving a resistance variable in steps of 1 ohm from 1 to 111111 ohms.

This box was checked from the standard resistances, but the higher coils were not used except when an approximate measurement only was possible. No appreciable error was found in the lower coils.

Preliminary experiments with a drum-wound bridge-wire showed that a sharp minimum could not be obtained at all positions on the bridge-wire, apparently owing to the unequal inductances of the two sections of the bridge, while a straight wire gave a good minimum at

all points. The bridge-wire employed therefore consisted of a length of constant wire stretched over a metre scale in the usual manner. To achieve increased accuracy of reading, two 50 ohm resistances were connected to the ends. Since the inductance of these coils balanced each other no difficulties due to unbalanced inductance were experienced from this source. By careful measurement it was ascertained that these coils corresponded to lengths of the bridge wire of 326.00 cms and 325.02 cms respectively. The bridge with the end coils in circuit therefore had an effective length of about 7,500 millimetres. Except in a few instances where it was impracticable, the measurements were made with the extension coils in circuit. The bridge wire was calibrated by means of the accurate resistances and a calibration curve drawn for the whole length of the wire, but, in practice the resistances were arranged so that the position of the minimum was near the centre except in a few cases where very high resistances required to be measured.

In order to balance out the difference between the capacity of the conductivity cell and of the resistance coils, variable air condensers in parallel with the standard resistance arm of the bridge were

used.

The connections in the bridge assembly were made with stout pieces of tinned copper wire and were kept as short as possible, while the leads to the cell were of constantan D.C.C. wire. These were taken to two mercury cups resting in the water of the thermostat connected with the electrode tubes by short lengths of copper wire, the ends of all these wires being cleaned and freshly amalgamated. The resistance of the leads and lengths of copper wire was then carefully measured and subtracted from the measured resistance of each solution.

Throughout the measurements, a uniform room temperature of about 20°C was maintained. By means of these precautions it is believed that any errors arising from thermoelectric effects at the various metal junctions were eliminated. This was further ensured by the use of a gas-heated water thermostat, the temperature being controlled to $\pm$.01° C.

With this apparatus the sound minimum did not, as a rule, extend over more than a fraction of a millimetre when resistances up to 10000 ohms were being measured corresponding to an accuracy greater than 0.01 per cent, while measurements of the same resistance at different points of the bridge usually

checked to about the same degree of accuracy, provided that these points were near the centre of the bridge-wire. Measurements of resistances lying between 10,000 and 100,000 ohms are accurate to about 0.1 or 0.2 per cent, while measurements of resistances higher than 100,000 ohms are accurate only to 1 or 2 per cent.

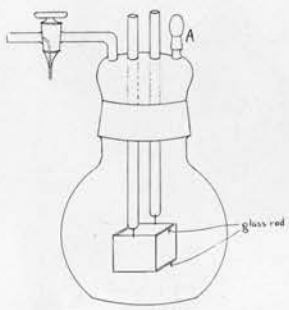
The Conductivity Cells:- Three cells were found necessary to cover the range of solutions investigated. These cells are described below.

Cell I is shown in figure 10. It consists of a short Pyrex tube closed by a rubber stopper which carries the electrode tubes. Since the tube is only about 4 or 5 inches long, little movement of the electrodes relative to each other can occur. In order to obviate this, however, the electrodes are sealed together with a piece of glass rod. This cell had a constant of about 0.9 and was used for solutions in water and 19.64 per cent alcohol whose concentrations were greater than about .01N.

Cells 2 & 3 were similar to that described by Hartley and Barrett [Trans. Chem. Soc. p 789 (1913)] The design of these cells is also shown in the figure. They were made of Pyrex glass. It will be seen that they consist of wide-necked flat bottomed flasks provided with externally ground caps, through which

Fig.10.

Cell 1.



Cells 2&3.

are sealed the electrode tubes. In addition, each cap is fitted with a tube provided with a three-way tap in order to be able to pass pure air through the cell, and contains an additional tube A with a cap through which are made additions of solution. The solution is stirred by rotating the cap. Whereas in Cell I the electrodes are set horizontally in the cell, in these cells they are vertical. In order to prevent any movement of the electrodes they are sealed together with short portions of Pyrex rod. Cell 2 had a capacity of about 100c.c.s, while the electrodes were about 2 cms. apart, its constant being about .14. This cell was used for the dilute aqueous solutions and for the more concentrated solutions in the solvents containing 89.92 and 46.62 moles per cent alcohol. Cell 3 possessed a capacity of about 300 ccs., while the electrodes were about 1 cm apart, its constant being about .07. The measurements in pure alcohol and the measurements in dilute solutions in the alcoholic solvents were taken in this cell. In all cases the electrodes were platinised and then heated to red-ness in the blow pipe to convert the platinum-black to grey platinum.

Device for preparing and preserving the mixed solvents:-

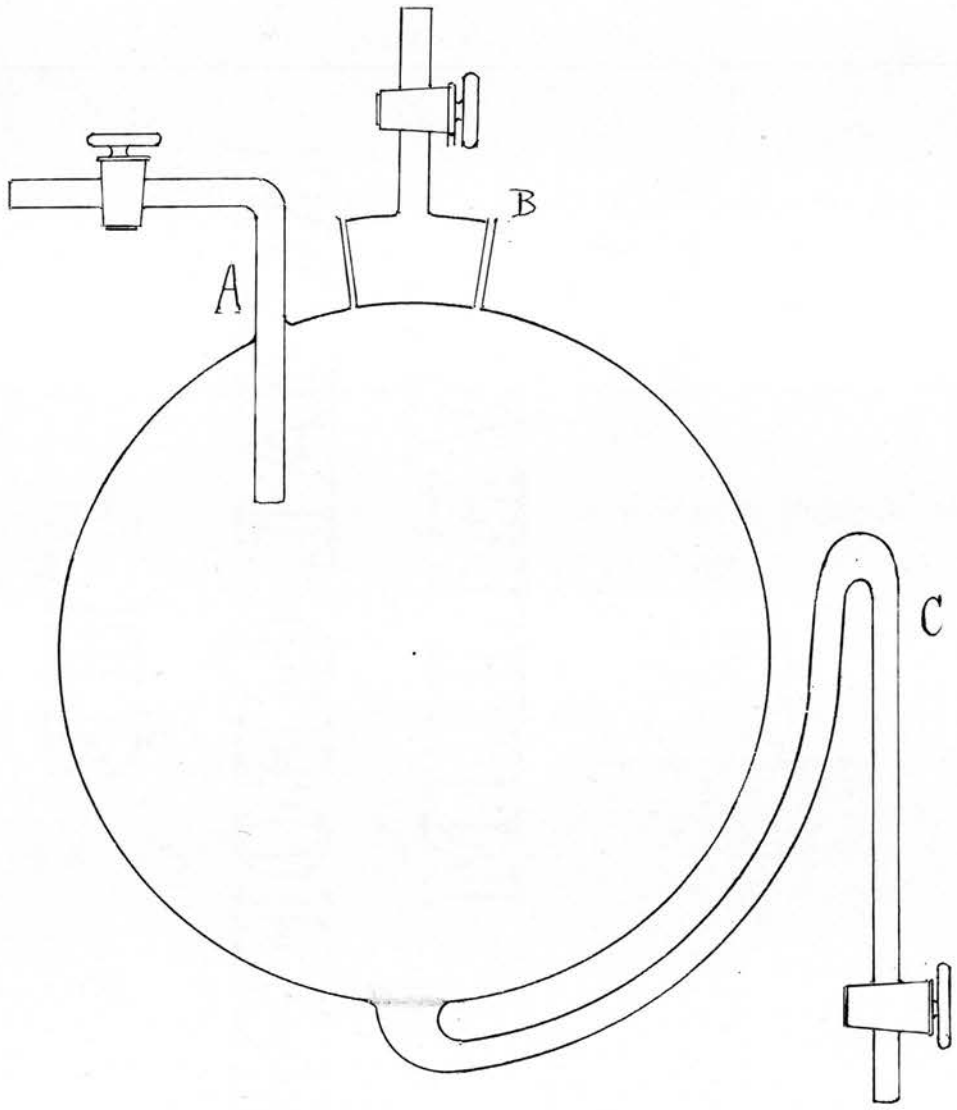
It is essential for accurate measurements in dilute

solution that the solvents shall possess a low specific conductivity, hence the mixed solvents must be protected from the air as far as possible. As mentioned above it is impracticable to make a solvent which is to contain accurately a predetermined proportion of alcohol without exposing the solvents to the ordinary air. It was therefore decided not to attempt to make up solvents containing exactly the same proportion of alcohol as those in Section I.

The apparatus used is shown in Figure 11. It consists of a Pyrex bulb of about 1 litre capacity. Through the upper portion of this bulb is sealed a glass tube A provided with a tap in order to admit pure air into the bulb. A cap B, also provided with a tap, is ground into the neck of the bulb and serves as a stopper, while the solvent is run out of the bent tube C sealed into the base of the bulb. The purpose of the bend in this tube is to hinder the diffusion of the liquid in contact with the tap into the bulk of the solvent, in case any contamination should arise from the tap. The bend also renders the bulb much more portable and easily weighed.

In making up a mixed solvent the following procedure was followed. The bulb, having been thoroughly cleaned, was dried by passing pure dry air

- Fig 11.-



- Device for preparing mixed solvents -

through it over-night. It was then weighed, the taps being kept closed. The tube A was connected to the air supply and some alcohol was run into the bulb. The stopper was then replaced, the taps closed and the bulb disconnected from the air supply and re-weighed. Approximately the correct amount of water to make the required solvent was now added in the same way and the bulb reweighed. The composition of the solvent was then calculated. It may be remarked here that, since the tap on the tube C is kept closed during the weighing process this tube does not fill with alcohol owing to air imprisoned between the tap and bulb. A little, is, however, forced by the pressure of the supernatant liquid into the tube. In order to mix this with the bulk of the liquid the air supply is connected to tube C, after the final weighing , and, on opening the tap B. the liquid is forced into the bulk of the solution, thus effecting thorough mixing. Finally, A is again connected to the pure air supply, the tap on B closed and the tap on C opened, when the tube C fills with liquid. The bulb is now kept permanently connected to the air supply by A and when solvent is required the tap on C is opened, the pressure of pure air forcing the solvent into the cell or vessel. It should be

mentioned here that the portion of solvent in the tube C was always rejected before filling the cells or vessels. The specific conductivities of the solvents prepared in this way are seen in Table V.

Procedure.

In the determination of the conductivities of the dilute solutions essentially the same method of procedure was followed as that used by Sir Harold Hartley and his co-workers in their work on conductivity measurements in dilute solution in ethyl and methyl alcohol.

The cell was thoroughly cleaned and then dried by passing a current of pure dry air through it overnight. It was then weighed, filled to the level of an etched mark on the cell with the pure solvent and reweighed. After remaining in the thermostat for about an hour, the specific conductivity of the pure solvent was measured. The conductivity of a series of solutions was now determined by making successive additions of weighed amounts of a stock solution of known concentration from a weighing pipette, measurements of the resistance being taken after each addition and being continued, in each case until the resistance was constant to about 1 part in 10,000.

After each addition the contents of the cell were stirred by rotating the cap and by shaking. Whenever the cell was opened by means of the little cap on A, in order to make an addition, pure air was passed over the solution by means of the inlet provided, so that the solution was not contaminated by contact with ordinary air. In this way the conductivities of solutions whose concentrations lay between $\frac{N}{10,000}$ and $\frac{N}{100}$ were determined. Seven additions were usually made in one run.

The stock solutions were made up by weighing. Since however zinc chloride is very hygroscopic, the weighing was carried out in a small stoppered distilling flask of about 75 ccs. capacity, the side tube of which was furnished with a tap so that pure dry air could be passed into the flask when required. In order to make up a stock solution for the pipette the following procedure was adopted.

The small flask was thoroughly cleaned and dried. The air was then displaced by pure dry air or else the flask was left in a desiccator containing phosphorus pentoxide overnight to dry the air inside it. The stopper was now inserted and the tap closed, these operations being performed in the desiccator and the flask was weighed. A small quantity of zinc

chloride was then rapidly transferred to the flask, the stopper re-inserted and the flask and contents reweighed. Approximately the amount of solvent necessary to make a thirtieth or twentieth normal solution was added, and the final weighing performed. When solution was complete the solution was sucked into the weighing pipette.

The weighing pipette was constructed from a short cylindrical bulb of Pyrex glass by sealing Pyrex taps above and below the bulb. Beyond the lower tap the tubing was drawn into a short thick capillary and a small glass cap was ground to fit this, the cap being removed only for the purpose of making additions to the solution in the cell.

The stock solutions were made up immediately before use and at once transferred to the pipette but no special precautions were taken to ensure that they were not exposed to the atmosphere beyond those mentioned. Since no more than 10 or 15 ccs. of solution in all were added to the solvent in the cell, any slight rise in the conductivity of the stock solutions occasioned by the momentary exposure to the air during transference from the flask to the weighing pipette must have been negligible.

It will be noted that the procedure described

above gives the concentrations in weight normalities.

In order to convert these to concentrations expressed in gram-equivalents per litre at 25° it was assumed that the stock solutions possessed the same density as the solvents, and that no appreciable changes of volume occurred on adding the stock solution to that in the cell. Density determinations at the commencement of the work indicated that inaccuracies arising from this assumption were within the experimental error. The densities of the mixed solvents used were determined in this laboratory by Miss Connell while the densities of the water and ethyl alcohol at 25°C were taken as 0.9971 and 0.7851 respectively.

These assumptions cannot however be made in the case of the concentrated solutions. A different method of procedure therefore was employed in the measurements with these solutions.

In the work on the concentrated solutions it has been assumed that the conductivities of the solutions were not sensibly affected by momentary exposures to the air. The following method was used to determine the conductivities of these solutions.

After the conclusion of a run of dilute solutions the cell was opened, and approximately the amount of zinc chloride required to make a normal solution was

rapidly added to the solution in the cell. The cap was now immediately replaced and pure air passed into the cell until solution of the zinc chloride was complete. The small cap was replaced and the cell left in the thermostat until the resistance of the solution became constant. The cell was now removed from the thermostat, opened, and about half the solution was poured into a clean dry flask and kept for analysis. Pure solvent was then run into the solution in the cell to make up the volume to about its previous value, the cap was replaced and the cell returned to the thermostat, pure air being again passed in. In this manner dilution was continued until a concentration of about .05 or .02N was reached, measurements of the resistance being continued each time until a constant bridge-reading was obtained.

In order to determine the concentration, a measured volume of each solution was analysed by the method mentioned in Section I. The volumetric apparatus employed was of certified accuracy.

It will be remarked that the concentrations determined by this method cannot be stated at a fixed temperature, while the concentrations of the dilute solutions are stated at 25°. The assumption that these are sensibly the same, however, involves no

greater inaccuracy than the experimental error in determining the concentrations by the method above viz. 0.1 or 0.2 per cent.

The Solvent Correction:- This has been applied by subtracting the measured specific conductivity of the pure solvent at the beginning of a run from the measured conductivity of each solution.

Determination of the Cell Constants:- The Cell constants have been determined at 25° employing Parker's 0.01N solution of potassium chloride. The data for this solution are given in the International Critical Tables Vol. VI p 230. It is made up by dissolving 0.74625 gms. of potassium chloride in 1000gms. of conductivity water, its specific conductivity at 25° being 0.0014078(9) r. ohms. In the original paper [Parker and Parker. J. Amer. Chem. Soc., 46, 312, (1924)] instructions for making up the solution are given.

Analytical Reagent potassium chloride was once recrystallised from conductivity water, drained and dried at 100°C in an electric oven. When a cell constant was to be determined, a little of the potassium chloride was transferred to a clean crucible and heated in the full flame of a Meker burner for about twenty minutes in order to complete the drying.

The crucible and contents were then allowed to cool in a desiccator over phosphorus pentoxide. About 1000 grammes of conductivity water were now weighed out into a Pyrex flask fitted with a clean rubber stopper. The calculated weight of potassium chloride was then weighed in a weighing bottle which had been thoroughly cleaned and dried inside and outside and the weighing bottle and contents were transferred to the flask of water. When solution was complete, the solution was poured into another clean dry Pyrex flask in case that the solution might dissolve glass from the weighing bottle on standing in contact with it. Parker weighs the potassium chloride on a watch glass and does not state how the potassium chloride was transferred to the vessel of water. The author's experience is, that unless the vessel in which the potassium chloride is weighed is also transferred to the flask of water, it is difficult to ensure that the last trace of potassium chloride is added to the solution. The cell constants were frequently determined during the course of the work and no sensible variation has been observed. The values which have been used throughout the calculations are:-

Cell 1 0.9311

Cell 2 0.1398(7)

Cell 3 0.07529

These figures represent the means of several concordant determinations. The specific conductivity of the water employed in making up the potassium chloride solutions was measured immediately before a determination and was added to the stated specific conductivity of the solution viz. 0.0014078(9)r. o.

Experimental Data.

The results of the measurements are given in Table V where k is the specific conductivity of the pure solvent in reciprocal megohms, C is the concentration in gram-equivalents per litre (See page 55) and Λ_c is the equivalent conductivity.

A few remarks may be made here on the accuracy of the results. In the first place, since the resistances of the solutions could, as a rule, be measured with an accuracy far exceeding that with which the concentrations could be determined, the accuracy of the values of Λ_c will depend on the accuracy to which the concentrations are known. In the concentrated solutions the results will therefore be accurate to about 0.1 or 0.2 per cent. In the dilute solutions, since the stock solutions were made up by weight , the accuracy should exceed this, except in the case of pure alcohol where the resistances of the dilute solutions were very high, (between 400,000ohms and 60,000ohms.)

Another factor which introduces an unavoidable error into the results is the solvent correction. As will be seen from the results the conductivity of zinc chloride in the alcoholic solutions is very low, so that the solvent correction is necessarily large in the most dilute solutions.

Table V.

Water.

k	C	$\sqrt{C}$	Λ_c
1.89	0.0002452	0.01566	122.4 *
0.99	0.0003116	0.01765	122.8
	0.001030	0.03209	119.8
	0.003181	0.05640	116.5
	0.005245	0.07243	115.4
	0.007451	0.08633	114.3
	0.01045	0.1022	112.8
1.10	0.01584	0.1258	110.3
	0.03169	0.1780	105.4
	0.06337	0.2517	99.47
	0.1016	0.3187	94.92
	0.2543	0.5043	85.19
	0.3091	0.5560	82.55
	0.5086	0.7132	74.69
	1.0171	1.008	60.91
	1.509	1.228	51.25

* A measurement from a previous run. The specific conductivity of the water was rather high.

Table V (continued).

19.64 Moles per cent alcohol.

k	C	$\sqrt{C}$	Λ_c
	0.00016844	0.01298	47.05
	0.00044559	0.02111	46.55
	0.0012845	0.03585	45.42
	0.0023836	0.04883	44.40
	0.0036797	0.06066	43.39
	0.0058026	0.07617	42.09
0.467	0.0071074	0.08431	41.50
	0.01760	0.1326	37.38
	0.06906	0.2628	29.85
	0.1889	0.4347	22.14
	0.4051	0.6365	16.19
	0.9257	0.9621	11.14

Table V (continued).

46.62 Moles per cent Alcohol.

k	C	$\sqrt{C}$	Λ_c
	0.0001942	0.01393	37.96
	0.0007493	0.02738	34.77
	0.0014426	0.03799	31.42
	0.0036615	0.06052	25.35
	0.0067148	0.08194	20.84
0.211	0.0099434	0.09972	17.98
	0.013267	0.1152	16.06
	0.06548	0.2559	7.156
	0.1296	0.3600	5.436
	0.2937	0.5420	4.079
	0.6226	0.7891	3.338
	1.4151	1.190	2.848

Table V (continued).

89.92 Moles per cent alcohol.

k	C	$\sqrt{C}$	Λ_c
0.0763	0.0003365	0.01834	4.098
	0.00094049	0.03067	2.472
	0.0026444	0.05142	1.699
	0.0046566	0.06825	1.341
	0.0072447	0.08511	1.126
	0.010978	0.1048	0.9546
	0.013586	0.1166	0.8805
	0.04354	0.2087	0.5877
	0.1176	0.3430	0.4876
	0.2424	0.4923	0.4587
	0.5488	0.7408	0.4511
	0.9968	0.9984	0.4601

Table V (continued).

100 Moles per cent alcohol.

k	C	$\sqrt{C}$	Λ_c
	0.0001766	0.01329	0.900
	0.0003563	0.01888	0.63(3)
	0.0008059	0.02839	0.430
	0.0018480	0.04299	0.290
	0.0031135	0.05581	0.257
	0.0047203	0.06871	0.217
0.029	0.0059658	0.07723	0.197
	0.02116	0.1455	0.1302
	0.05208	0.2282	0.1111
	0.1178	0.3433	0.1063
	0.2598	0.5098	0.1086
	0.5118	0.7154	0.1203

In the case of the most dilute solution investigated in pure alcohol, an error of 1 per cent in measuring the specific conductivity of the pure solvent would involve an error of 1 part in 700. In the other solvents, however, the errors arising from the solvent correction would be less than 1 part in 1000.

Finally, the method employed in determining the cell constants is open to the objection that it is difficult to weigh out a predetermined amount of potassium chloride accurately and to transfer it to a flask without introducing small errors.

Summarising, it may be asserted that, with the exception of the data for the most dilute solutions in pure alcohol where errors of the magnitude of 1 or 2 per cent may occur, the results are accurate to 0.1 or 0.2 per cent, and in many cases will possess a greater accuracy than this. The main sources of error arise from the nature of zinc chloride itself and are therefore unavoidable, while any errors in the determination of the cell constants will affect only the absolute values of the results. Since, however, the chief purpose of the research is to ascertain the effect of alcohol on the ionisation of zinc chloride, the relative values of the conductivities in the various solvents possess a greater interest than the absolute values.

The absence of errors of any considerable magnitude is shown by the smoothness of the curves obtained when Λ_c is plotted against the square root of c, (Figure 12)

The results agree well with those obtained by Gibbons and Getman (Loc. Cit.,) in water, but the author's results in pure alcohol are considerably lower than those obtained by these investigators. (Figure 14). Since hydrolysis of the zinc chloride, atmospheric contamination, or alcohol which was not sufficiently dry, would all tend to raise the conductivity values, it appears as if some of these factors had influenced the results of these authors.

Discussion.

Figure 12 is a plot of the equivalent conductivities against the square root of the concentration. In order to show the curve for the aqueous solutions on the same diagram as the others, the scale for this curve has been halved as indicated.

Perhaps the most interesting feature of the results is the remarkable drop in the conductivity of the solutions caused by the first additions of alcohol. This may be seen in Figure 13 where the values of Λ_c in the different solvents, at constant concentration, are plotted against the composition of the solvent. The data for this plot are shown in Table VI and have been obtained by graphical interpolation from/

Table VI (over)

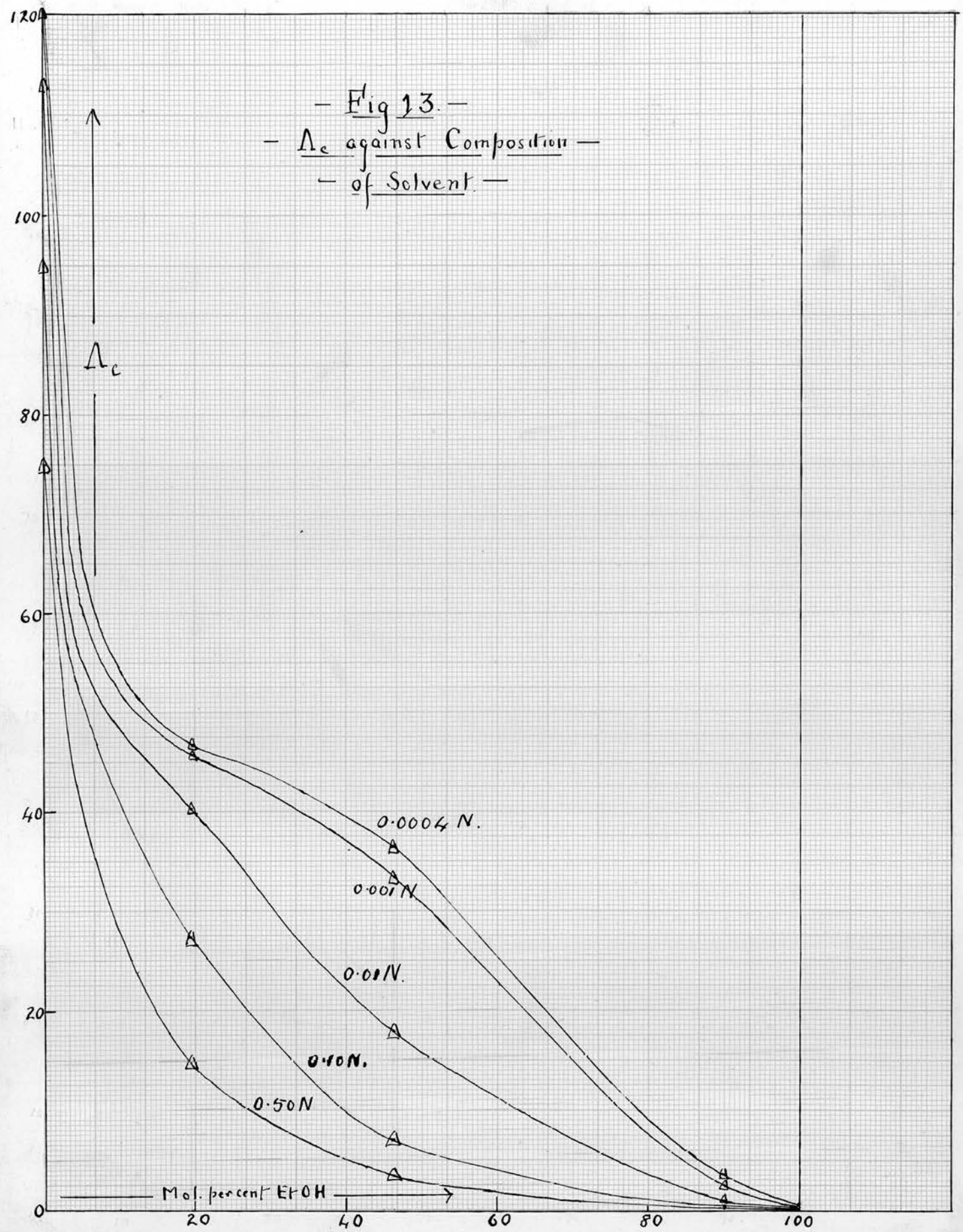

— Fig 13. —
— Λ_c against Composition —
— of Solvent —
120
100
80
60
40
20
0
Λ_c
0·0004 N.
0·001 N
0·01 N.
0·10 N.
0·50 N
Mol. per cent EtOH
20
40
60
80
100

Table VI.

Approximate values of Λ_c in the different solvents at constant concentration.

C gm-equivalents per litrs.	Composition of solvent (mols. per cent. alcohol)				
	0	19.64	46.62	89.92	100
0.0004	122.0	46.65	36.60	3.60	0.60
0.001	120.5	45.75	33.40	2.40	0.39
0.01	113.0	40.20	17.90	0.98	0.17
0.10	95.0	27.30	6.00	0.50	0.11
0.50	75.0	14.70	3.40	0.45	0.12

large scale plots of Λ_c against the square root of the concentration for each solvent. It will be noted that the curves descend very steeply between 0 and 19.64 moles per cent alcohol after which the fall is less steep. At a concentration of about 0.01N an inflexion appears and becomes more marked as the concentration decreases until the general character of the curves is similar to those obtained when the free energies were plotted against composition of the solvent. (Figure 7). The resemblance of the two diagrams is interesting, although, as was shown in Section I, the steep fall of the free energies with the first additions of alcohol is not

due to the repression of the ionisation of the zinc chloride indicated by the rapidly falling conductivity on addition of alcohol, seen in Figure 13.

The results for aqueous solutions yield a curve which is slightly convex to the axis of $\sqrt{c}$, as will be seen from figure 12. This curvature persists to a small extent in the dilute solutions but is, nevertheless, not so great as to prevent an approximate value of the equivalent conductivity at infinite dilution (Λ_0) being arrived at by extrapolation to zero concentration. When this is carried out by means of a large-scale plot of the values for the seven most dilute solutions, we obtain $\Lambda_0 = 125.5 \pm 0.5$, while the limiting slope is about 175. Onsager [Phys. Z., 27, p.388 (1926); 28, 277 (1927); Trans. Faraday Soc., 23, 341, (1927)] has shown that the conductivity of an electrolyte in dilute solution can be represented by the equation

$$\Lambda = \Lambda_0 - \left\{ \frac{0.986.10^6}{(DT)^{\frac{3}{2}}} \omega \Lambda_0 + \frac{29.0}{(DT)^{\frac{1}{2}}\eta} (z_1 + z_2) \right\} \sqrt{(z_1 + z_2)c}$$

where D is the dielectric constant of the solvent

T is the absolute temperature.

η is the viscosity of the solution.

c is the equivalent concentration

and $w = z_1 z_2 \frac{2q}{1 + \sqrt{q}}$

where $q = \frac{z_1 z_2 (\Lambda_1^\circ + \Lambda_2^\circ)}{(z_1 + z_2)(z_2 \Lambda_1^\circ + z_1 \Lambda_2^\circ)}$

z_1 and z_2 being the valencies of cation and anion respectively and Λ_1° and Λ_2° their zero concentration mobilities.

When $\Lambda_1^\circ + \Lambda_2^\circ = \Lambda_\circ$ is taken as 125.5, the mobility of the chloride ion at 25°C as 75.30 (Davies, conductivity of solutions, p 181) and the remaining values inserted in the equation, it becomes

$$\Lambda = \Lambda_\circ - 172.1\sqrt{c}$$

The experimental value of 175 for the limiting slope is thus in reasonable agreement with that predicted by the theory. viz. 172.1. It must be pointed out, however, that this agreement only holds up to a concentration of about 0.001N. At concentrations greater than this the experimental slope is less than that given by the above equation. It may however be reasonably assumed that in solutions of concentration less than 0.001N, in water, zinc chloride is practically completely dissociated according to the scheme

$$ZnCl_2 = Zn^{++} + Cl' + Cl'$$

The curves for 19.64 moles per cent and 46.62 moles per cent alcohol present interesting features. In both cases there is a linear region which extends from zero concentration up to 0.01N in the solvent

containing 19.64 moles per cent alcohol, while in the case of the solvent with the higher alcohol content, the curve ceases to be linear with $\sqrt{c}$ above about 0.005N. The limiting values of the slopes and the values of Λ_0 obtained by extrapolation are shown in Table VII.

Table VII.

Composition of solvent. mol. per cent. alcohol.	Λ_0	Limiting slope
0	125.5	175
19.64	48.25	80.9
46.62	42.10	275

The value of the limiting slope in 19.64 moles per cent alcohol is seen to be much less than that in water, while the slope in 46.62 moles per cent alcohol is much greater than in water. Since the data necessary for the calculation of the Onsager slopes of these two curves are not available at present, the interpretation of the results cannot be attempted in the meantime. For a similar reason the degrees of dissociation of zinc chloride in these solvents cannot, at present, be calculated.

– Fig 14 –

Λ_c against $\sqrt{c}$

⊙ German & Gibbons

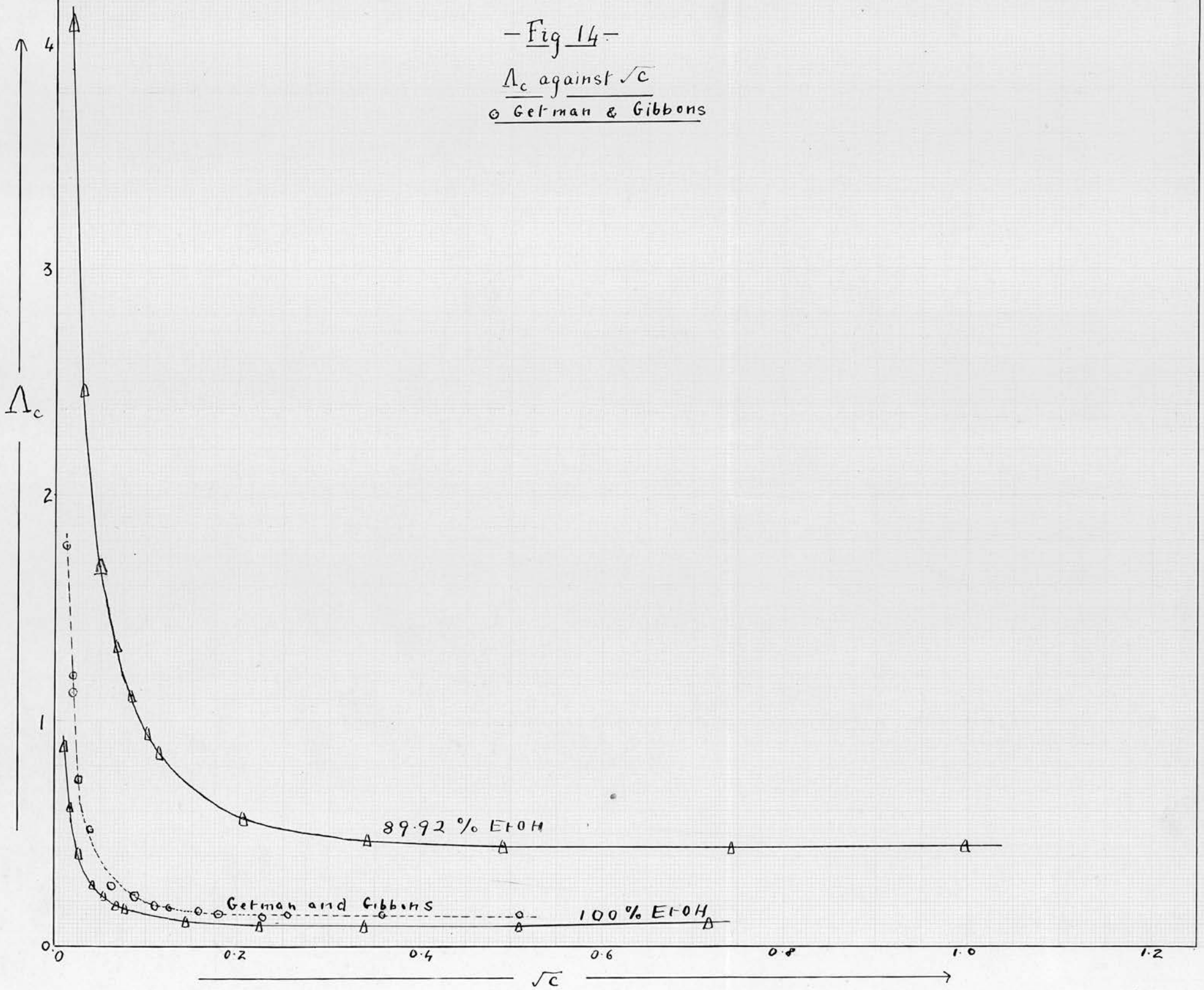


Figure 14 shows a large-scale plot of Λ_c against $\sqrt{c}$ for the solvents containing 89.92 and 100 moles per cent alcohol. The results show the existence of a small, but definite minimum, in each case. In pure alcohol this occurs at a concentration of about 0.1N while in 89.92 moles per cent alcohol it takes place at about 0.5N. Obviously, these curves are not capable of extrapolation to infinite dilution. The extreme smallness of the values of Λ_c in these solvents, however, indicates that zinc chloride has practically ceased to be an electrolyte. Even in hundredth normal solution in pure alcohol the specific conductivity is about equal to that of good distilled water. (viz. about 2×10^{-6} r.o.). It will be recalled that this result was inferred from the electromotive force measurements in Section I.

While it is unfortunate that degrees of dissociation cannot at present be calculated, the results are nevertheless of interest as illustrating the transition of a substance from a strong electrolyte in one solvent to a non-electrolyte in another solvent.

Summary.

(1) The electrical conductivities of zinc chloride have been determined at 25°C in a concentration range of $\frac{N}{10,000}$ to N in a series of solvents containing 0, 19.64, 46.62, 89.92 and 100 moles per cent alcohol.

(2) In the solvents containing 0, 19.64 and 46.62 moles per cent of alcohol, values for the limiting slopes and for the equivalent conductivity at infinite dilution have been obtained.

(3) The results in aqueous solutions indicate that in solutions whose concentrations are not greater than about 0.001N, zinc chloride is almost completely dissociated as a uni-bivalent electrolyte.

(4) In 89.92 moles per cent alcohol and in pure alcohol the results demonstrate that zinc chloride is practically a non-electrolyte.

In conclusion I wish to express my indebtedness to the Department of Scientific and Industrial Research for a grant, during the tenure of which this research was carried out, and to the Moray Fund for a grant which helped to defray the cost of part of the apparatus. I also wish to tender thanks to Dr. J.A.V. Butler for many helpful suggestions and for his deep interest in the work.